REACTION OF ALKYL AND SILALKYL HALIDES WITH ORGANOMETALLICS

by

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A Thesis presented for the degree of

Doctor of Philosophy

Department of Chemistry

The University of Aston in Birmingham

June 1976

SUMMARY

We have observed contrary to previous observations that (3-bromopropyl)triphenylsilane reacts with magnesium to give reasonable yields of the corresponding Grignard reagent. The same Grignard reagent is produced by metal exchange from the reaction of (3-bromopropyl)triphenylsilane with alkyl Grignards. In contrast methyltriphenylsilane is the major product from the reaction of bromomethyltriphenylsilane with alkyl Grignard reagents in ethereal solvents, however in benzene some metal transfer takes place and the Grignard reagent Ph_3SiCH_2MgBr is obtained in about forty per cent yield. Such metal transfer reactions are not observed with similar alkyl halides and must arise due to the enhanced carbanion stability in the silicon systems.

Chloromethyltriphenylsilane with sodium in alcohol undergoes a rearrangement which involves migration of a phenyl group from the silicon atom to the adjacent carbon atom. It has been suggested that such rearrangements are promoted by nucleophilic participation at silicon, our results indicate an electron transfer type mechanism and the intermediacy of a carbanionic species. Similar rearrangements are observed in the reaction of chloromethyltriphenylsilane with n-butyllithium and silver chloride and when iodomethyltriphenylsilane is treated with potassium hydroxide in aqueous ethanol.

$[^2H_3]$-Methyltriphenylsilane undergoes exchange with t-butyllithium. TMEDA and the lack of exchange observed previously with the light compound is probably due to the fact that the organometallic intermediate picks up hydrogen from the solvent and there is no observable change.

This work was carried out between 1972 and 1976 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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ACKNOWLEDGEMENTS

I would like to express my most profound gratitude to my supervisor, Dr. A.W.P. Jarvie, for her constant advice, kindness and encouragement during my research studies at Aston and to Dr. A. Holt for his help and advice. I am also grateful to Dr. R.J. Rowley, for his help and consideration during my first years research. I would like to thank the members of the laboratory staff in the Chemistry Department, in particular Mr. E.J. Hartland, Mrs. V. Clenton, Mrs. M. Evans, Mr.M.C.Perry, Mr. M. Houghton and Mr. R.J.Butler, for their kind help in the spectral and analytical work.

I wish to thank the British Council for meeting the cost of my registration fees.

Finally, I would like to thank Mr. K.W.S. Kularatna, Mr. H.M.N. Bandara, Dr. C.R. Westwood and Mr. P. Harris for their advice.

To my parents

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GENERAL INTRODUCTION

Compounds of the type $Me_3Si(CH_2)_nX$ (n = 1 or 3) react normally with lithium[1] and magnesium[2] and give good yields of the corresponding organometallic compounds. Rather surprisingly it has been found that the corresponding triphenyl-compounds behave abnormally. Brook[3] observed that neither the triphenylsilylmethyl Grignard nor lithium compounds can be prepared by direct reaction of triphenylsilylmethyl bromide with the metal. Gilman et al.[4] reported that only an 8% yield of the carboxylic acid $Ph_3Si(CH_2)_3CO_2H$ could be isolated from the carbonation of the corresponding Grignard reagent in diethylether.

Brook's[3] observation that direct reaction of Ph_3SiCH_2X with magnesium is not possible was surprising, since the Grignard reagent $Ph_2\underset{H}{\overset{|}{Si}}CH_2MgX$ can be prepared by direct reaction with the metal[5]. It also seemed unlikely that a triphenylsilyl group would have such a powerful influence on the reactivity of a gamma halide function that it would prevent Grignard formation. Because these previous observations appeared anomalous we decided to reinvestigate the reactions of the alpha- and gamma-haloalkyltriphenylsilanes with magnesium.

It had been observed previously that $Ph_3SiCH_2CH_2MgX$ compounds can be prepared by an exchange type process[6].

$$Ph_3SiCH_2CH_2Br + RMgX \longrightarrow PH_3SiCH_2CH_2MgX$$

We also investigated this route for the preparation of the corresponding alpha and gamma compounds.

We found that the alpha and gamma compounds like the beta compound[6], underwent metal transfer with Grignard reagents. Kharasch and Reinmuth[7] state that Functional Exchange between an organic halide and an organomagnesium compound is a relatively rare reaction and the general feeling one derives from a study of the literature is that the exchange reaction between Grignard reagents and organic halides does not take place to any extent except with highly electronegative halides or with highly polar solvents. However a number of the reports appear contradictory[7,18,19] and we could not be sure whether the haloalkyltriphenylsilanes were behaving abnormally compared with other alkyl halides in these exchange reactions. Because of this we decided to look at the reactions of some comparable alkyl halides with Grignard reagents.

Triphenylsilylmethyl compounds also show anomalous behaviour in metalation reactions. It has been reported that no metalation occurs in the reaction of methyltriphenylsilane[3] with n-butyllithium tetramethylethylenediamine (TMEDA) complex whereas fairly rapid metalation is observed with Me_4Si, Me_3SiCH_2Cl and a number of other similar reagents[8,9]. It has been reported by Brook[3] that the Ph_3SiCH_2Li compound, when formed by exchange, is unstable in ether solvents and fairly rapidly picks up a hydrogen from the solvents. We thought it was possible that the apparent lack of exchange with methyltriphenylsilane in the metalation reaction was due to the fact that the organometallic intermediate picked up hydrogen from the solvent and there was no observable change. To establish if exchange in fact occurred we prepared $[^2H_3]$methyltriphenylsilane Ph_3SiCD_3 and studied its exchange with n-butyllithium TMEDA and a number of other reagents.

The reaction of chloromethyltriphenylsilane Ph_3SiCH_2Cl with sodium in alcohol has also been studied and it has been found that this compound undergoes a rearrangement comparable with that observed for the aryldimethylsilylmethyl chlorides, $PhMe_2SiCH_2Cl$ with sodium ethoxide in ethanol[10]:-

$$PhMe_2SiCH_2Cl \xrightarrow[EtOH]{EtO^-} Me_2Si(OEt)_2 + PhCH_3$$

$$EtO^- \rightarrow SiMe_2(Ph) - CH_2 - Cl \longrightarrow EtOSiMe_2CH_2Ph + Cl^-$$

$$EtOSiMe_2CH_2Ph \xrightarrow[EtO^-]{EtOH} Me_2Si(EtO)_2 + PhCH_3$$

It has been suggested that this rearrangement is promoted by nucleophilic reagents.

We found that the rearrangement proceeds rapidly with dissolving metal solutions but does not occur to any extent with the preformed alkoxides. This would suggest that the rearrangement is not promoted by nucleophiles but proceeds via an electron transfer mechanism.

This rearrangement is not observed in the reaction of Ph_3SiCH_2X with n-butyllithium but can be promoted by the addition of silver chloride to the reaction mixture.

CHAPTER I

REACTIONS OF TRIPHENYLSILYLALKYLHALIDES AND ALKYL HALIDES WITH MAGNESIUM AND GRIGNARD REAGENTS

I The Reaction of 3-Bromopropyltriphenylsilane with Magnesium

The reaction between 3-bromopropyltriphenylsilane and magnesium in dry diethylether gave, after quenching the reaction mixture with deuterium oxide, propyltriphenylsilane (12%), 3-d_2-propyltriphenylsilane (60%) and 1,6-bis(triphenylsilyl)hexane (20%).

$$Ph_3SiCH_2CH_2CH_2Br + Mg \xrightarrow{D_2O/H^+} \begin{cases} Ph_3SiCH_2CH_2CH_3 & (12\%) \\ Ph_3SiCH_2CH_2CH_2D & (60\%) \\ [Ph_3SiCH_2CH_2CH_2]_2 & (20\%) \end{cases}$$

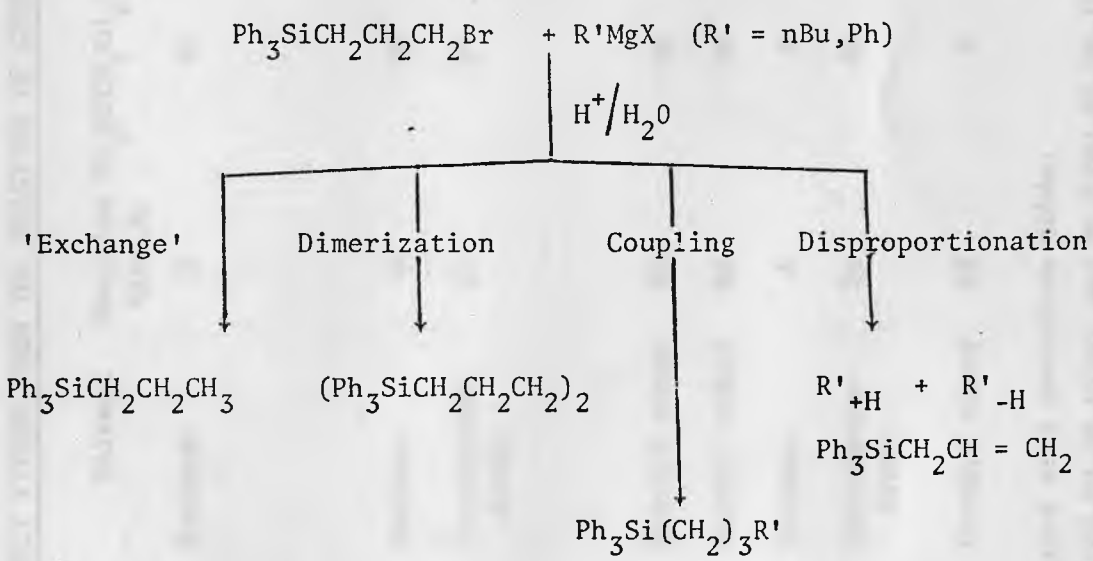
Carboxylation of the reaction products yielded, 3-carboxypropyl-triphenylsilane (50%), 1,6-bis(triphenylsilyl)-hexane (24%) and propyltriphenylsilane (16%)

$$Ph_3SiCH_2CH_2CH_2Br + Mg \xrightarrow{CO_2/H^+} \begin{cases} Ph_3SiCH_2CH_2CH_2COOH & (50\%) \\ PH_3SiCH_2CH_2CH_3 & (16\%) \\ [Ph_3SiCH_2CH_2CH_2]_2 & (24\%) \end{cases}$$

These results indicate that (3-bromopropyl)triphenylsilane reacts with magnesium in a normal straight forward manner and it is difficult to understand why previous workers[4] detected such a low yield of the Grignard reagent for this system.

II Reaction of (3-Bromopropyl)triphenylsilane with Grignard Reagents

These reactions were investigated in diethylether, benzene and tetrahydrofuran (THF). The results of these experiments are recorded in Table 1. All the reactions were carried out under standard conditions, using excess organometallic reagents as described in the experimental section. The main types of products obtained from the reaction of (3-bromopropyl)triphenylsilane with Grignard reagents are given in the following scheme.



It should be noted at this point, that the term 'exchange' is used simply for convenience and is not intended to imply any mechanistic pathway. The so called 'exchange process' may have occurred by true halogen-metal exchange:-

TABLE 1. PRODUCT YIELDS FROM THE REACTION OF GRIGNARD REAGENTS WITH [3-BROMOPROPYL]TRIPHENYLSILANE

Grignard(RMgBr)	Solvent	Reaction time.h.	$Ph_3SiCH_2CH_2CH_3$	$Ph_3Si(CH_2)_6SiPh_3$	$Ph_3Si(CH_2)_3Br$	$Ph_3Si(CH_2)_3R$	Other Products (%)
Bu^nMgBr	Benzene	3	49	20	0	0	$Ph_3SiCH_2CH=CH_2$(4), I(7)Ph-Ph(1) $CH_3CH_2CH_2CH_3$(67), $CH_3CH_2CH=CH_2$(38)
Bu^nMgBr[a]	Benzene	3	55[b]	14	0	0	$Ph_3SiCH_2CH=CH_2$(4),I(5)
Bu^nMgBr	Tetrahydro-furan	24	54	17	0	0	$Ph_3SiCH_2CH=CH_2$(8),I(14) $CH_3CH_2CH_2CH_3$(72), $CH_3CH_2CH=CH_2$(35)
Bu^nMgBr	Diethyl ether	48	66	8	0	0	$Ph_3SiCH_2CH=CH_2$(6),I(9)
Bu^nMgBr[a]	Diethyl ether	48	70[c]	7	0	0	
PhMgBr	Benzene	4	0	0	77	22	
PhMgBr	Tetrahydro-furan	24	40	5	11	8	$Ph_3SiCH_2CH=CH_2$(6),I(12) Ph-Ph (45)
PhMgBr	Diethyl ether	48	0	0	96	4	

[a]Reaction terminated with deuterium oxide;

[b]Mixture of $Ph_3SiCH_2CH_2CH_2D$(46) and $Ph_3SiCH_2CH_2CH_3$(9)

[c]Mixture of $Ph_3SiCH_2CH_2CH_2D$(50) and $Ph_3SiCH_2CH_2CH_3$(20)

Product I = 2,3-benzo-1,1-diphenyl-sila-2-cyclohexene.

$$Ph_3SiCH_2CH_2CH_2Br + R'MgBr \rightleftharpoons Ph_3Si(CH_2)_3MgBr + R'Br$$

$$\downarrow H^+/H_2O$$

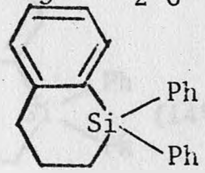
$$Ph_3SiCH_2CH_2CH_3$$

but the hydrocarbon product might equally well have arisen by formation of the radical $Ph_3SiCH_2CH_2CH_2\bullet$ followed by proton abstraction from the solvent etc. or by direct reduction of the 3-bromopropyltriphenylsilane by the Grignard reagent. To determine whether the $Ph_3SiCH_2CH_2CH_3$ was derived from a Grignard intermediate or by hydrogen abstraction from the solvent the reactions were terminated with D_2O, product analysis indicates that Grignard formation was about 50% in both ether and benzene solvents

$Ph_3SiCH_2CH_2CH_2Br$ + nBuMgBr

D_2O

Benzene		Diethylether	
$Ph_3SiCH_2CH_2CH_3$	(9%)	$Ph_3SiCH_2CH_2CH_3$	(20%)
$Ph_3SiCH_2CH_2CH_2D$	(46%)	$Ph_3SiCH_2CH_2CH_2D$	(50%)
$Ph_3Si(CH_2)_6SiPh_3$	(14%)	$Ph_3Si(CH_2)_6SiPh_3$	(7%)



(5%) (I)*

$Ph_3SiCH_2CH = CH_2$ (4%)

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* For the compound (I) we received an authentic sample of the cyclic compound 2,3-benzo-1,1-diphenyl-sila-2-cyclohexene from Professor H. Gilman and the identity of the cyclic compound was established by mixed melting point and comparison of spectra.

This reaction like the comparable reaction with the alpha (vide infra) and beta compounds[6] is a metal transfer process, we did not detect exchanged halide in these reactions so it is not a true halogen metal exchange reaction.

(a) The Reaction of 3-Bromopropyltriphenylsilane with n-Butylmagnesium Bromide

The percentages of different products depended upon the solvents employed as indicated below:

$Ph_3SiCH_2CH_2CH_2Br$ + nBuMgBr

(H_2O/H^+)

THF (24 hours)

$Ph_3SiCH_2CH_2CH_3$ (54%)

$Ph_3Si(CH_2)_6SiPh_3$ (17%)

$Ph_3SiCH_2CH = CH_2$ (8%)

$CH_3CH_2CH_2CH_3$ (72%)

$CH_3CH_2CH = CH_2$ (35%)

Diethylether (48 hours)

$Ph_3SiCH_2CH_2CH_3$ (56%)

$Ph_3Si(CH_2)_6SiPh_3$ (8%)

$Ph_3SiCH_2CH = CH_2$ (6%)

Benzene (3 hours)

$Ph_3SiCH_2CH_2CH_3$ (49%)

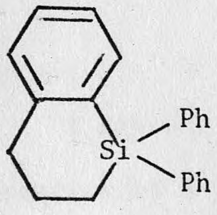
$Ph_3Si(CH_2)_6SiPh_3$ (20%)

$Ph_3SiCH_2CH = CH_2$ (4%)

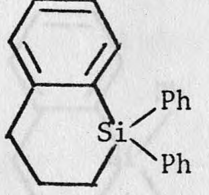
Ph-Ph (1%)

$CH_3CH_2CH_2CH_3$ (67%)

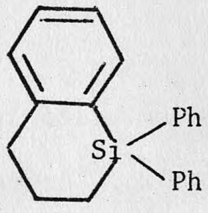
$CH_3CH_2CH = CH_2$ (38%)



(14%)



(9%)



(7%)

(b) The Reaction of 3-Bromopropyltriphenylsilane with Phenylmagnesium Bromide

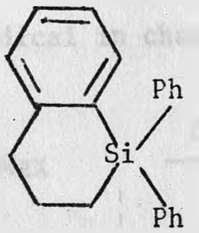
The reaction of 3-bromopropyltriphenylsilane with phenylmagnesium bromide in the same three solvents has also been studied. Wurtz coupling was the only process observed in the reactions in benzene and in diethylether. Whereas a combination of Wurtz coupling, dimerized compound, 1,6-bis(triphenylsilyl)hexane and exchange product was obtained in THF. With the reactions in benzene and in ether a considerable amount of the starting material $Ph_3SiCH_2CH_2CH_2Br$ remained unreacted. The yield of coupling product in benzene was greater than in diethylether

$Ph_3SiCH_2CH_2CH_2Br$ + PhMgBr

(H_2O/H^+)

Benzene (4 hours) | THF (24 hours) | Diethylether (48 hours)

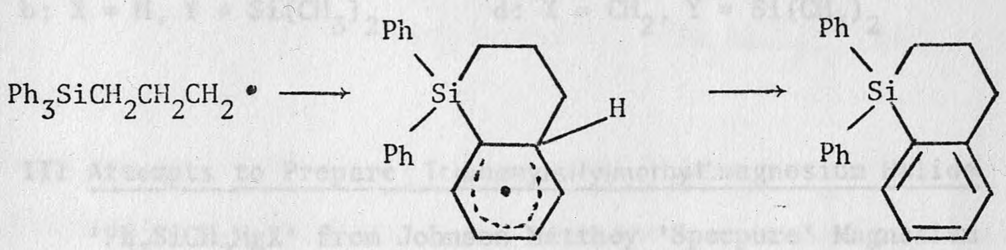
Benzene (4 hours)	THF (24 hours)	Diethylether (48 hours)
$Ph_3SiCH_2CH_2CH_2Br$ (77%)	$Ph_3SiCH_2CH_2CH_2Br$ (11%)	$Ph_3SiCH_2CH_2CH_2Br$ (96%)
$Ph_3SiCH_2CH_2CH_2Ph$ (22%)	$Ph_3SiCH_2CH_2CH_2Ph$ (8%)	$Ph_3SiCH_2CH_2CH_2Ph$ (4%)
	$Ph_3SiCH_2CH_2CH_3$ (40%)	
	$Ph_3Si(CH_2)_6SiPh_3$ (5%)	
	$Ph_3SiCH_2CH=CH_2$ (6%)	
	Ph-Ph (45%)	



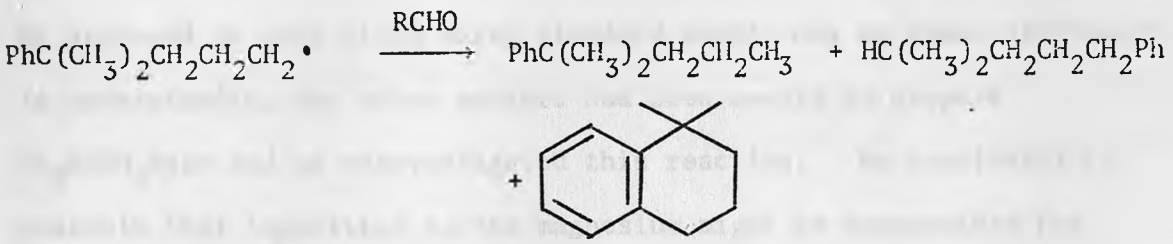
(12%)

The olefinic product $Ph_3SiCH_2CH = CH_2$, the coupling product biphenyl (Ph-Ph) and the cyclic product, 2,3-benzo-1,1-diphenyl-sila-2-cyclohexene wasonly obtained in THF from the reaction of $Ph_3SiCH_2CH_2CH_2Br$ with phenylmagnesium bromide, PhMgBr.

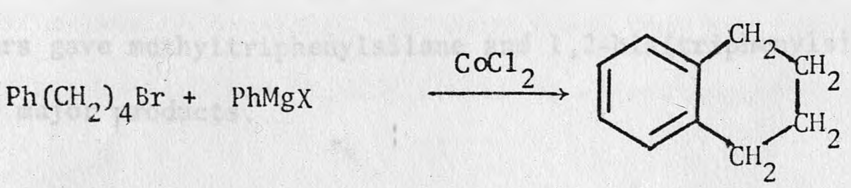
In these reactions of the 3-bromopropyltriphenylsilane with Grignard reagents, the cyclic compound[68] 2,3-benzo-1,1-diphenyl-sila-2-cyclohexene formed presumably arises from a free radical cyclisation since it is not formed from the Grignard itself.



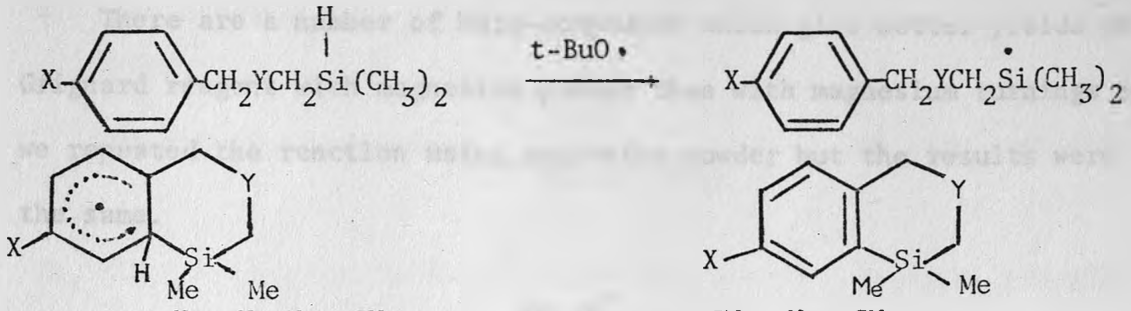
Cyclisation reactions involving homolytic aromatic substitution by carbon radicals are well known. Winstein[12] reported a reaction involving both migration of phenyl group and cyclisation.



A similar cyclisation takes place in the cobalt chloride catalysed reaction of 4-phenylbutylbromide with aromatic Grignard[11], a reaction which is known to be radical in character.



A similar cyclisation of silyl radicals has been reported recently[13].



a: X = H, Y = CH_2 c: X = CH_3, Y = CH_2

b: X = H, Y = $Si(CH_3)_2$ d: X = CH_2, Y = $Si(CH_3)_2$

III Attempts to Prepare Triphenylsilylmethylmagnesium Halide 'Ph_3SiCH_2MgX' from Johnson Matthey 'Specpure' Magnesium Crystals and Powder Magnesium

Having prepared the Grignard reagent from 3-bromopropyltriphenylsilane in good yield, and knowing that the Grignard Ph_2SiCH_2MgBr could be produced in good yield using standard conditions we found difficulty in understanding why other workers had been unable to prepare Ph_3SiCH_2MgBr and we reinvestigated this reaction. We considered it possible that impurities in the magnesium might be responsible for the failure to obtain the Grignard so we attempted the preparation using Johnson Matthey 'specpure' magnesium crystals. Carbonation of the reaction mixture using either THF or diethylether as solvents for 18 hours gave methyltriphenylsilane and 1,2-bis(triphenylsilyl)ethane as the major products.

$$Ph_3SiCH_2Br + (\text{Johnson Matthey 'Specpure'})Mg \xrightarrow[\text{18 hours}]{CO_2/H^+} \begin{matrix} (Ph_3SiCH_2)_2 & (30\%) \\ Ph_3SiCH_3 & (70\%) \end{matrix}$$
Diethylether

There are a number of halo-compounds which give better yields of Grignard reagent with magnesium powder than with magnesium turnings so we repeated the reaction using magnesium powder but the results were the same.

$$Ph_3SiCH_2Br + Mg(\text{powder}) \xrightarrow[\text{12 hours}]{CO_2/H^+} \begin{matrix} Ph_3SiCH_3 & (65\%) \\ (Ph_3SiCH_2)_2 & (34\%) \end{matrix}$$
Diethylether

Sometimes carbonation is a poor method of derivatisation so we deuteriated the reaction mixture, but mass spectral analysis indicated that no deuterium was incorporated in the products.

$$Ph_3SiCH_2Br + Mg(\text{powder}) \xrightarrow[\text{12 hours}]{D_2O} \begin{matrix} Ph_3SiCH_3 & (70\%) \\ (Ph_3SiCH_2)_2 & (27\%) \end{matrix}$$
Diethylether

$$Ph_3SiCH_2Br + (\text{Johnson Matthey 'Specpure'})Mg \xrightarrow[\text{12 hours}]{D_2O} \begin{matrix} Ph_3SiCH_3 & (68\%) \\ (Ph_3SiCH_2)_2 & (30\%) \end{matrix}$$
Diethylether

The preparation of the Grignard was then attempted using iodomethyltriphenylsilane, the same products were obtained in comparable yields using either magnesium powder or Johnson Matthey 'specpure' magnesium crystals. We have found that the reactions of iodomethyltriphenylsilane Ph_3SiCH_2I with an excess magnesium powder

in dry diethylether one at reflux temperature for 1/2 hour and another for 18 hours at room temperature gave, on terminating the reactions with deuterium oxide, 80-90% of methyltriphenylsilane. No deuterium has been detected in any of the products.

$$Ph_3SiCH_2I + Mg(\text{powder}) \xrightarrow[\text{Diethylether}]{D_2O} Ph_3SiCH_3 \quad (80\text{-}90\%)$$

$$Ph_3SiCH_2I + (\text{Johnson Matthey 'Specpure'})Mg \xrightarrow{D_2O} Ph_3SiCH_3 \quad (80\text{-}90\%)$$

Neglecting the presence of a small quantity of compound other than Ph_3SiCH_3 and $(Ph_3SiCH_2)_2$, the relative proportions of these two compounds in the final product after carbonation were Ph_3SiCH_3 (60-80%) and $(Ph_3SiCH_2)_2$ (20-35%).

$$Ph_3SiCH_2I + Mg(\text{powder}) \xrightarrow[\text{Diethylether}]{CO_2/H^+} \begin{matrix} Ph_3SiCH_3 & (60\text{-}80\%) \\ (Ph_3SiCH_2)_2 & (20\text{-}35\%) \end{matrix}$$

The similar reaction using Johnson Matthey 'Specpure' magnesium crystals in dry diethylether at reflux temperature for 1/2 hour gave, after carbonation, methyltriphenylsilane Ph_3SiCH_3 (68%) and 1,2-bis-(triphenylsilyl)ethane $(Ph_3SiCH_2)_2$ (30%) (These percentages were calculated neglecting the presence of a small quantity of a compound which could not be identified).

$$Ph_3SiCH_2I + (\text{Johnson Matthey 'Specpure'})Mg \xrightarrow[\substack{30 \text{ min.} \\ \text{Diethylether}}]{CO_2/H^+} \begin{matrix} Ph_3SiCH_3 & (68\%) \\ (Ph_3SiCH_2)_2 & (30\%) \end{matrix}$$

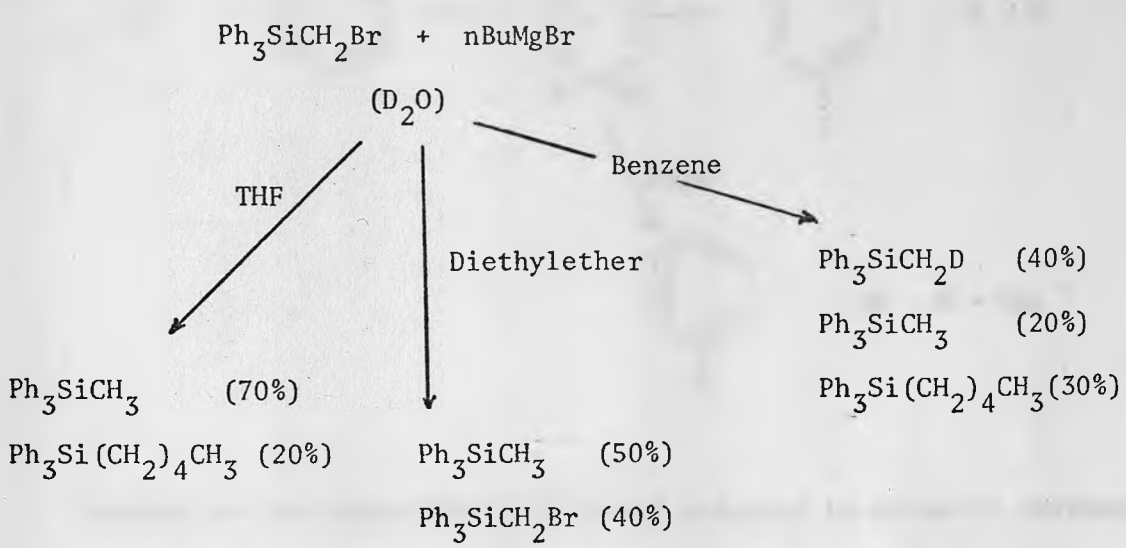
It has been reported by Huang and Wang[14] that the Grignard can be obtained from chloromethyltriphenylsilane and magnesium. This reaction was reinvestigated by Brook[3] who found he could not repeat the work, after the continuous failure with the bromo and iodo compounds we did not repeat the reaction with the chloro compound.

It is difficult to understand why the Grignard Ph_3SiCH_2MgX cannot be prepared when closely related compounds in which electronic effects must be very similar can be obtained readily. It would appear that whatever intermediates are formed they react very rapidly with the solvent. Brook[3] found that the Ph_3SiCH_2Li compounds were stable for several hours in ether solvents. We found that although the iodo compound Ph_3SiCH_2I reacted very rapidly with magnesium (reaction complete in 1/2 hour) we still could not isolate any products derived from an organometallic intermediate, so the organomagnesium compound if formed must react very rapidly with the solvent.

IV The Reaction of Bromomethyltriphenylsilane with n-Butylmagnesium Bromide

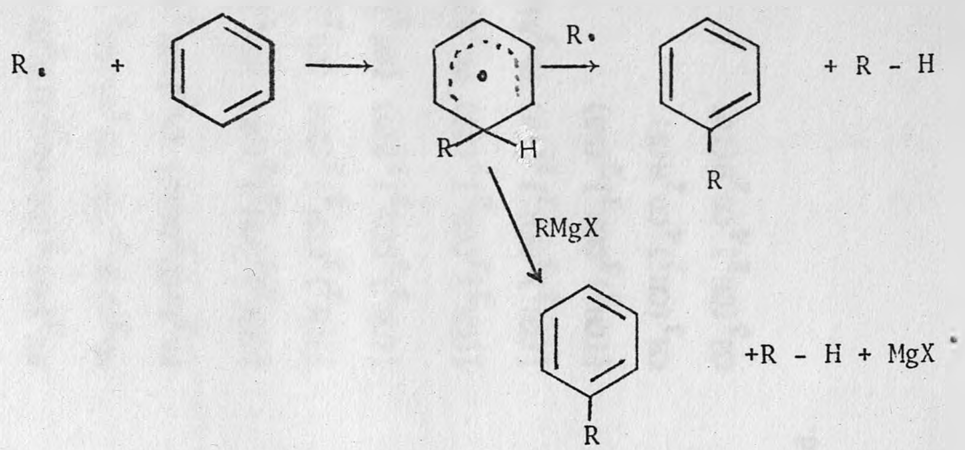
Since the attempt to prepare the Grignard reagent Ph_3SiCH_2X (X = Br, I) directly from α-halogenomethyltriphenylsilane with magnesium was unsuccessful, it was decided to investigate whether it was possible to prepare the Grignard reagent via an 'exchange' process, which had already been shown to be successful in the beta[6] - and gamma-system (from this thesis).

The reaction of bromomethyltriphenylsilane with n-butylmagnesium bromide was performed in diethylether, THF and benzene. Methyltriphenylsilane and n-amyltriphenylsilane were obtained as the major products after terminating the reactions with deuterium oxide. A summary of results is given below:



Deuteriation studies showed that about 40% of the Grignard reagent Ph_3SiCH_2MgBr was produced in benzene as shown from the formation of Ph_3SiCH_2D obtained. The coupling product of n-amyltriphenylsilane $Ph_3Si(CH_2)_4CH_3$ was found in THF and in benzene but not in diethylether when only unreacted bromomethyltriphenylsilane was obtained beside methyltriphenylsilane. In the etheral solvents (THF and ethylether) the main product was methyltriphenylsilane which was formed entirely by hydrogen abstraction from the solvent or other component of the reaction mixture. (Table 2.). The hydrogen abstraction product methyltriphenylsilane (20% Ph_3SiCH_3) which was observed in benzene, may arise from the incomplete removal of the ether solvent used in the initial preparation of the Grignard reagent

(n-butylmagnesium bromide) and if careful attention were paid to removal of the ethereal solvent, good yields of the Grignard Ph_3SiCH_2MgX might be obtained by metal exchange in benzene. The Ph_3SiCH_3 might also be formed in a process of the type



Studies on the formation of Grignard reagents in aromatic solvents[71] suggest that this type of process could be occurring on the magnesium surface and similar reactions could take place in the main body of the solvent.

The formation of hydrogen abstraction products in all of the solvents does not require that radical intermediates are involved in these reactions. Brook[3] observed for the analogous organolithium system, the organometallic rather than a radical intermediate may abstract hydrogen from the solvent. There is evidence given by Boak and Gowenlock[15] that trimethylsilylmethyl carbanions are more stable than the radicals. The difference in stability between the carbanion and the radical would be expected to be even greater in the triphenylsilylmethyl system, and carbanion formation should occur readily.

TABLE 2. PRODUCTS FROM THE REACTION OF ALKYL GRIGNARD REAGENTS WITH VARIOUS ALKYL HALIDES

RMgX	RX	Solvent	Time h	Products (%)
Bu^nMgBr[a]	Ph_3SiCH_2Br	diethyl ether	24	Ph_3SiCH_3(50) Ph_3SiCH_2Br(40)
Bu^nMgBr[a]	Ph_3SiCH_2Br	tetrahydrofuran	24	Ph_3SiCH_3(70) $Ph_3Si(CH_2)_4CH_3$(20)
Bu^nMgBr[a]	Ph_3SiCH_2Br	benzene	24	Ph_3SiCH_2D(40) Ph_3SiCH_3(20) $Ph_3Si(CH_2)_4CH_3$(30)
Neopent MgBr	EtI[b]	diethyl ether	5	$[(CH_3)_3CCH_2]_2$(30) $(CH_3)_3CCH_2I$(20) EtI(50)
Neopent MgBr	MeI[b]	diethyl ether	5	$[(CH_3)_3CCH_2]_2$(30) $(CH_3)_3CCH_2I$(20)
Neopent MgBr	BuI[b]	diethyl ether	5	$[(CH_3)_3CCH_2]_2$(20) $(CH_3)_3CCH_2I$(10) BuI(40)
Neopent MgBr	Ph_3SiCH_2Br[b]	diethyl ether	24	$[(CH_3)_3CCH_2]_2$(25) Ph_3SiCH_2Br(35)
Neopent MgBr	Ph_3SiCH_2Br[b]	diethyl ether	5	$[(CH_3)_3CCH_2]_2$(10) Ph_3SiCH_2Br(70)
Neopent MgBr	EtBr[b]	diethyl ether	5	$[(CH_3)_3CCH_2]_2$(30)
Neopent MgBr	BuBr	diethyl ether	5	$CH_3(CH_2)_4CO_2H$(5)
Neopent MgBr	BuI	diethyl ether	5	$CH_3(CH_2)_4CO_2H$(10)

[a] Reaction terminated with deuterium oxide were not analysed.

[b] Products derived from organic halides.

V Halogen-Metal Exchange

A halogen-metal exchange is a reaction of an organometallic compound with an organic halide:-

$$RX + R'M \rightleftharpoons RM + R'X$$

For organo-lithium compounds[16] the equilibrium constants are determined principally by the relative electronegativities of the radicals R and R'.

$$R'X + RLi \rightleftharpoons R'Li + RX$$

Metal-atoms prefer to reside with the more electronegative R-group.

Equilibrium constants have been determined for a number of systems, and at one time it was thought that these constants might be used as a measure of carbanion stability[17].

The equilibrium data of Appleguist and O'Brien[17] is summarized in Table 3.

Text books on Grignard reaction generally state that:

$$RX + R'MgX \rightleftharpoons R'X + RMgX$$

TABLE 3. EQUILIBRIUM CONSTANTS FOR $RLi + R'I \rightleftarrows RI + R'Li$ [17]

R'	R	K_{obsd}[b] Ether, -70°	40% Ether-60% pentane -70°	40% Ether-60% pentane, -23°	Pentane, -23°
Vinyl	Phenyl	258 ± 11			
Phenyl	Cyclopropyl	9.55 ± 0.46			
Cyclopropyl	Ethyl		333 ± 23		
Ethyl	*n*-Propyl	2.38 ± 0.20[c]	2.56 ± 0.10		
n-Propyl	Isobutyl	5.11 ± .28	5.45 ± .22	7.96 ± 0.33	7.77 ± 0.22
Isobutyl	Neopentyl	7.49 ± .28	(6.92 ± .70)[e]		21.59 ± 1.47
Isobutyl	Cyclobutyl		35.3 ± 3.5		
Neopentyl	Cyclobutyl		5.10 ± 0.11[d]		
Cyclobutyl	Cyclopentyl		5.82 ± 1.22		

[a] Except where otherwise indicated, data for each reaction were collected in two runs, one from each direction.

[b] Errors shown are average deviations of all points after equilibrium had been reached.

[c] There were four runs, two in each direction.

[d] There was only one run, a reaction of neopentyllithium with cyclobutyl iodide.

[e] Calculated from the isobutyl-cyclobutyl and nopentyl-cyclobutyl K_{obsd}'s.

The exchange reaction between Grignard reagents and organic halides does not take place to any extent except with highly electronegative halides or with highly polar solvents.

$$\begin{matrix} R^F X \\ Ar^F X \end{matrix} \quad + \quad RMgX \quad \longrightarrow \quad \begin{matrix} R^F MgX \\ Ar^F MgX \end{matrix} \quad + \quad RX$$

The exact nature of these processes (whether these are equilibrium processes, as with the organolithium compounds) has not been established.

In 1964 Zakharkin and co-workers[18] studied the reaction of organic halides with Grignard reagents at low temperatures (0-5°C) in dimethoxyethane (DME) which is more polar than diethylether. The main reaction was halogen-metal exchange. They also found that the 'exchange' reaction depended on the effect of both the polarity of the solvent and the nature of the halide. Essentially they observed that very little exchange (5.7%) took place in diethylether, the extent of the exchange becoming significant in DME and increasing with the electronegativity of the halides in the order Cl < Br < I, alkylbromide greater than arylbromide.

TABLE 4. EXTENT OF EXCHANGE IN THE $C_5H_{11}MgBr$-CH_3I SYSTEM IN VARIOUS ETHERS[18]

(One hour at 0°)

No.	Solvent	$\%CH_3MgX$
1	Diethylether	5.7
2	Diethoxyethane	6.6
3	Methoxyethane	12.7
4	Diglyme	15.8
5	Tetrahydrofuran	17.5
6	Dimethoxyethane	38.5

TABLE 5. INFLUENCE OF HALIDE IN ALKYL HALIDE AND ORGANOMAGNESIUM COMPOUND ON THE EXTENT OF EXCHANGE IN THE RMgX-R'X SYSTEM [18]

No.	RMgX	R'X'	Solvent	% R'MgX
1[a]	$C_5H_{11}MgBr$	C_2H_5Cl	dimethoxyethane	0.2
2[a]	$C_5H_{11}MgBr$	C_2H_5Br	dimethoxyethane	1.0
3[a]	$C_5H_{11}MgBr$	C_2H_5I	dimethoxyethane	15.0
4[a]	$C_5H_{11}MgCl$	CH_3I	tetrahydrofuran	25.5
5[a]	$C_5H_{11}MgBr$	CH_3I	tetrahydrofuran	17.5
6[a]	$C_5H_{11}MgI$	CH_3I	tetrahydrofuran	20.3
7[b]	$C_5H_{11}MgBr$	C_6H_5Br	dimethoxyethane	0
8[b]	$C_5H_{11}MgI$	C_6H_5I	dimethoxyethane	52.0
9[b]	$C_5H_{11}MgBr$	*p*-BrC_6H_5Br	dimethoxyethane	6.8
10[b]	$C_5H_{11}MgBr$	*p*-ClC_6H_4Br	dimethoxyethane	12.0
11[b]	$C_5H_{11}MgBr$	*p*-ClC_6H_4I	dimethoxyethane	71.5
12[b]	$C_5H_{11}MgBr$	*p*-FC_6H_4Cl	dimethoxyethane	5.5
13[c]	$C_5H_{11}MgBr$	α-$C_{10}H_7I$	dimethoxyethane	74.4

[a] 0°, 1h; [b] 20°, 3h; [c] 20°, 2h; α-naphthoic acid was obtained (m.p.159°), yield 74.4%

TABLE 6. THE DEPENDENCE OF THE EXTENT OF EXCHANGE ON THE CHARACTER OF THE RADICAL R'(0°, 1h)[18]

No.	RMgX	R'X'	Solvent	% R'MgX
1	$C_5H_{11}MgBr$	CH_3I	tetrahydrofuran	17.5
2	$C_5H_{11}MgBr$	C_2H_5I	tetrahydrofuran	6.0
3	$C_5H_{11}MgBr$	*n*-C_3H_7I	tetrahydrofuran	2.5
4	$C_5H_{11}MgBr$	*iso*-C_3H_7I	tetrahydrofuran	2.5
5	$C_5H_{11}MgBr$	*n*-C_4H_9I	tetrahydrofuran	1.5
6	$C_5H_{11}MgBr$	*tert*-C_4H_9I	tetrahydrofuran	1.0
7	$C_5H_{11}MgBr$	$C_6H_5CH_2Cl$	tetrahydrofuran	1.0
8	$C_8H_{17}MgBr$	CH_3I	dimethoxyethane	20.7

On the basis of their results, they concluded that the mechanisms of exchange reactions for organomagnesium and organolithium compounds are very similar and that differences between them are due to the fact that organolithium compounds are stronger nucleophiles and consequently more suitable for exchange. The extent of the exchange reaction was determined by measuring the yields of carboxylic acids formed so it is impossible to determine whether they were observing true halogen metal exchange.

$$RX + R'MgX \rightleftharpoons RMgX + R'X$$

or merely metal exchange

$$RX + R'MgX \longrightarrow RMgX + ?$$

as we observed for the reactions of Grignard reagents with the haloalkylsilicon compounds.

In contrast to Zakharkin's results Korshunov and Batalov[19] found that CH_3CH_2MgBr and CH_3CH_2Br underwent complete exchange in diethylether at 40°C and again in direct contrast Kharasch and Reinmuth[7] state Functional exchange between an organic halide and an organomagnesium halide is a relatively rare reaction. It is difficult to decide from the literature whether exchange does or does not occur with Grignard reagents and organic halides.

The alkylhalosilanes behave abnormally in halogen-lithium exchange reactions. Applequist and O'Brien[17] report that exchange occurs between alkyllithium compounds and alkyliodides but there is no exchange with alkyl bromides, only random coupling, whereas

Brook[3] found that triphenylsilylmethyl bromides undergo rapid halogen-metal exchange with alkyllithium reagents. We were interested in finding out whether the exchange reactions of the alkylhalosilanes with Grignard reagents were in any way special, we were unable to decide from literature reports whether exchange was a common reaction with alkyl halides and Grignard reagents, so we decided to reinvestigate these reactions.

Reaction of Grignard Reagents with Organic Halides

Reactions were carried out under standard conditions using excess organometallic reagents, as described in the experimental section. They were performed in diethylether at room temperature for various times. The results of these experiments are recorded in Tables 2, 7 and 8.

(a) Reaction of Neopentylmagnesium Bromide with Organic Halides

We examined the reaction of neopentylmagnesium bromide (RMgX) with alkyl and aryl halides (R'X)

[where R' = methyl-, ethyl-, n-butyl-, n-octyl-,
phenyl-, triphenylsilylmethyl-,
and X = bromide-, iodide-]

The experiments were carried out at room temperature. The reactions of the neopentyl Grignard reagent with methyl iodide and ethyl iodide gave good yields of neopentyl iodide (halogen exchange product) and 1,2-bis(trimethyl)ethane (dimerized product).

Similarly the dimerized product, $[(CH_3)_3CCH_2)_2$ was the only product from the reactions between alkyl bromide (ethyl and n-octyl bromide) with this Grignard reagent. In the reactions with bromomethyltriphenylsilane the dimerized product $((CH_3)_3CCH_2)_2$ was the only product derived from the Grignard reagent.

None of the exchange product, neopentyl iodide was observed in the reaction with iodo-benzene.

All the results are shown in Table 2 and 7.

$$(CH_3)_3CCH_2MgBr + CH_3I \longrightarrow (CH_3)_3CCH_2I \quad (20\text{-}30\%)$$
$$CH_3CH_2I \qquad [(CH_3)_3CCH_2]_2 \quad (10\text{-}30\%)$$

$$(CH_3)_3CCH_2MgBr + CH_3CH_2Br \longrightarrow \text{no halogen exchange}$$
$$CH_3(CH_2)_7Br \qquad [(CH_3)_3CCH_2]_2 \quad (20\text{-}30\%)$$

$$(CH_3)_3CCH_2MgBr + Ph_3SiCH_2Br \longrightarrow [(CH_3)_3CCH_2]_2 \quad (10\text{-}25\%)$$
$$Ph_3SiCH_2Br \quad (35\text{-}70\%)$$

TABLE 7. THE SEARCH FOR ALKYL/ARYL HALIDES FORMATION IN THE REACTION OF ALKYL/ARYL GRIGNARD REAGENTS WITH VARIOUS ALKYL/ARYL HALIDES AT ROOM TEMPERATURES

Grignard Reagent RMgX	Alkyl/Aryl Halide R'X'	; Solvent	Time (hour)	R'X. Formed by Halogen-Exchange	
Neopent MgBr	CH_3I	diethylether	18	$(CH_3)_3CCH_2I$	(25%)
Neopent MgBr	CH_3CH_2I	diethylether	18	$(CH_3)_3CCH_2I$	(35%)
Neopent MgBr	CH_3CH_2Br	diethylether	18	$(CH_3)_3CCH_2Br$	(0%)
Neopent MgBr	PhI	diethylether	18	$(CH_3)_3CCH_2I$	(0%)
Neopent MgBr	$CH_3(CH_2)_7I$	diethylether	18	$(CH_3)_3CCH_2I$	(60%) uncertain
Neopent MgBr	$CH_3(CH_2)_7Br$	diethylether	18	$(CH_3)_3CCH_2Br$	(0%)
Bu^nMgBr	CH_3I	diethylether	18	$CH_3(CH_2)_3I$	(25%)
Bu^nMgBr	CH_3CH_2Br	diethylether	18	$CH_3(CH_2)_3Br$	(0%)
$CH_3(CH_2)_5MgBr$	CH_3I	diethylether	18	$CH_3(CH_2)_5I$	(0%)
PhMgBr	CH_3I	diethylether	18	PhI	(0%)

Carbonation of these reactions indicated that metal exchange product was formed in low yield in the reactions with methyl iodide, n-butyl iodide and n-butyl bromide, as shown from Table 8.

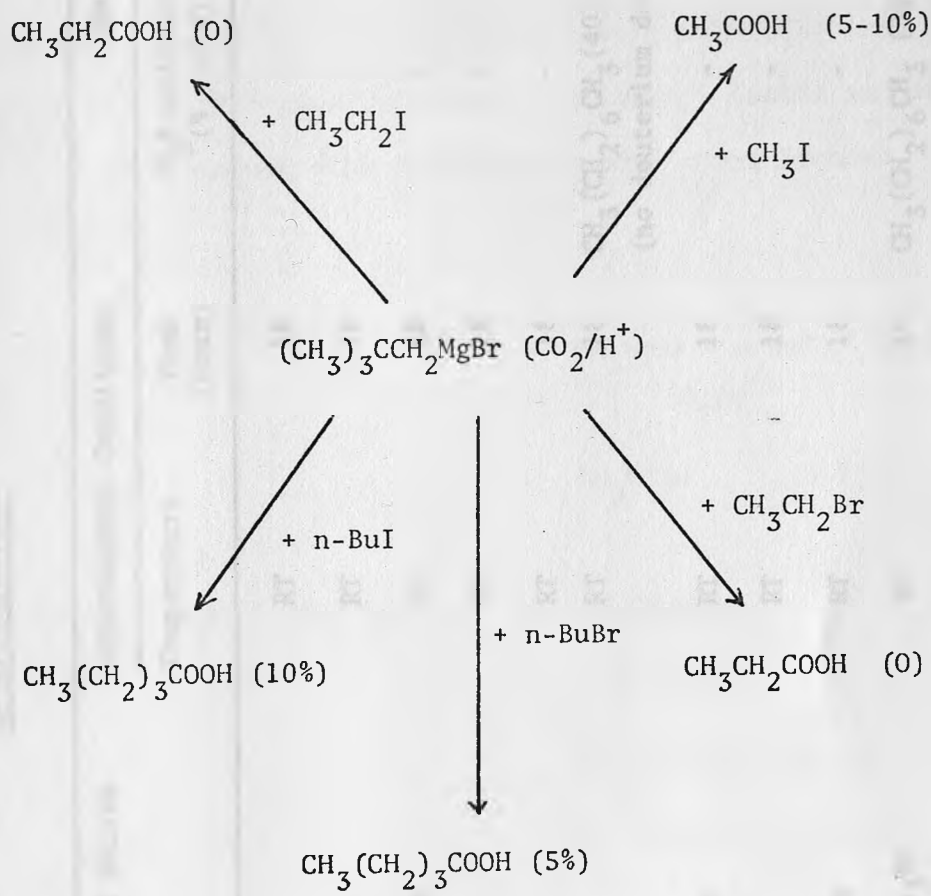


TABLE 8. THE ATTEMPTED METALATION OF THE REACTION OF ALKYL/ARYL GRIGNARD REAGENTS WITH VARIOUS ALKYL/ARYL HALIDES IN DIETHYLETHER

Grignard Reagent RMgX	Alkyl/Aryl Halide RX	Experimental Conditions		Method of Termination		
		Temperature	Time (hour)	D_2O addition (% yield)	CO_2 Addition (% yield)	
Neopent MgBr	CH_3I	RT	18	-	CH_3COOH	(5-10)
Neopent MgBr	CH_3CH_2I	RT	18	-	CH_3CH_2COOH	(0)
Neopent MgBr	CH_3CH_2Br	RT	18	-	CH_3CH_2COOH	(o)
Neopent MgBr	Bu^nBr	RT	18	-	$CH_3(CH_2)_3COOH$	(5)
Neopent MgBr	Bu^nI	RT	18	-	$CH_3(CH_2)_3COOH$	(10)
Neopent MgBr	n-Oct.I	RT	18	$CH_3(CH_2)_6CH_3$ (40) (no deuterium detected)	-	
Neopent MgBr	n-Oct.Br	RT	18	-	$CH_3(CH_2)_7COOH$	(0)
Bu^nMgBr	CH_3I	RT	18	-	CH_3COOH	(15)
Bu^nMgBr	CH_3CH_2Br	RT	18	-	CH_3CH_2COOH	(3)
Bu^nMgBr	$CH_3(CH_2)_7Br$	RT	18	$CH_3(CH_2)_6CH_3$ (30) $CH_3(CH_2)_6CH_2D$ (5)[a]	-	
Bu^nMgBr	PhI	RT	18	-	PhCOOH	(0)

[a] Identify by Mass spectra.

(b) Reaction of n-Butylmagnesium Bromide with Organic Halide

The halogen exchange product n-butyl iodide 25% was observed in the reaction of n-butylmagnesium bromide with methyl iodide, but no exchange was observed with ethyl bromide.

Carbonation of the reactions gave acetic acid (15%) from the reaction of n-butylmagnesium bromide with methyl iodide and propionic acid (3%) was obtained from the reaction with ethyl bromide (see Table 8).

$$CH_3(CH_2)_3MgBr + CH_3I \longrightarrow CH_3MgBr + n\text{-}BuI \quad (20\text{-}30\%)$$

$$\downarrow \; CO_2/H^+$$

$$CH_3COOH \quad (5\text{-}15\%)$$

$$CH_3(CH_2)_3MgBr + CH_3CH_2Br \longrightarrow CH_3CH_2MgBr$$

$$\downarrow \; CO_2$$

$$CH_3CH_2COOH \quad (\sim 5\%)$$

no halogen exchange

No halogen exchange product was obtained in the reaction of phenylmagnesium bromide with methyl iodide.

The carbonation reaction is not a very satisfactory method of derivatisation as it is a rather inefficient process, and the work up of reactions involving the lower aliphatic acids is difficult, and we thought this might explain the poor yields of the metal exchange products (Table 8).

However, termination with deuterium oxide of the reaction between the n-butylmagnesium bromide and n-octyl bromide again gave only 5% metal exchange (Table 8).

From these results we would conclude that in the reaction of Grignard reagents with organic iodides halogen exchange occurs fairly readily with alkyl iodides, no such exchange occurs with bromides. Metal exchange of the type we found with the haloalkyltriphenylsilane does not appear to occur to any extent with the other primary alkyl halides which we studied. This would suggest that the triphenylsilylalkyl derivatives form rather more stable carbanions than is normally observed with primary alkyl systems.

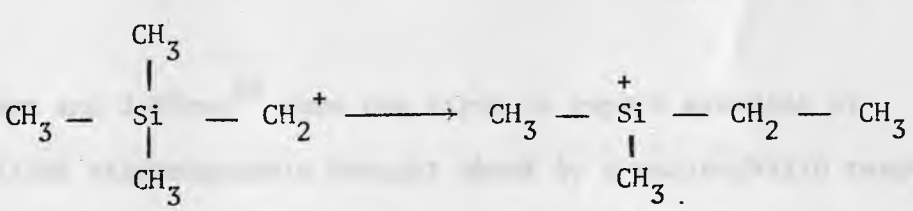
CHAPTER II

REARRANGEMENT

Introduction

There are several examples of intramolecular migrations of alkyl groups from a silicon-atom to an adjacent carbon-atom induced by electron-deficiency at the latter, the rearrangements being of the Wagner-Meerwein type[20,21,22] which involves the formation of a carbonium ion.

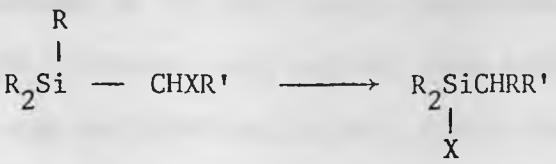
e.g.



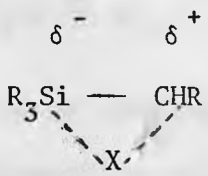
Recently O'Brien and co-worker[23] have suggested that because silicon can react via a pentaco-ordinated state that these reactions may proceed by an 'inverse ylide' mechanism and have obtained good kinetic evidence for the intermediacy of an 'inverse ylide' in the SbF_5 catalysed rearrangement of 2-chloro-2-trimethylsilylpropane.

(Nu = nucleophile) Products

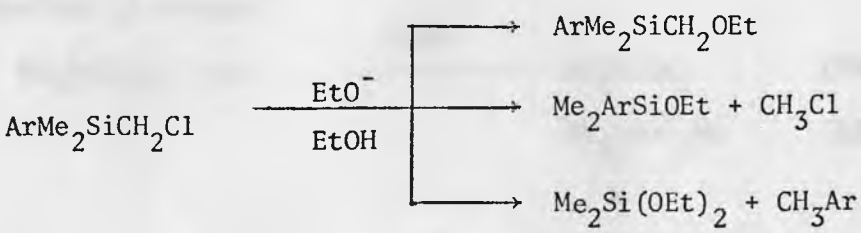
The non-catalysed equivalent of this rearrangement has been investigated by Bassindale and his co-workers[24] who found that certain α-substituted organo silanes undergo the following thermal rearrangement.



They measured a number of kinetic parameters and the migratory aptitudes of both X and R and proposed that the arrangement was best explained by a mechanism involving initial migration of X to silicon, to form an 'inverse ylide':



Eaborn and Jeffrey[10] were the first to report examples of organosilicon rearrangements brought about by a nucleophilic reagent and the first involving aryl groups. Thus aryldimethylsilylmethyl chlorides, $ArMe_2SiCH_2Cl$, on treatment with sodium ethoxide in ethanol give rise to toluene derivatives, $ArCH_3$, together with products of substitution at carbon and of cleavage of Si - CH_2Cl bonds:-



It was suggested that the toluene derivatives arose from the cleavage of silicon-benzyl bonds formed by intramolecular migration of the aryl group from silicon to a neighbouring carbon atom under the influence of nucleophilic attack of ethoxide ion at silicon. Electron withdrawal in the aryl group facilitates rearrangement, so $p\text{-}ClC_6H_4SiMe_2CH_2Cl$ reacts more rapidly than $ArSiMe_2CH_2Cl$. They suggested through nucleophilic attack, the silicon-atom is more negative in the highest energy state than in the initial state.

Kumada and co-workers[25,26] showed that trimethylsilyl groups also migrate under these conditions,

$$EtO^- + Me_2Si(SiMe_3)-CH_2-Cl \longrightarrow EtOSiMe_2CH_2SiMe_3 + Cl^-$$

and that this kind of rearrangement occurs generally with alkoxides NaOR in the corresponding alcohol ROH, where R = Me, Et, and Pr^i, and with sodium phenoxide in benzene[26].

$$Me_3SiSiMe_2CH_2Cl + PhO^- \longrightarrow PhOSiMe_2CH_2SiMe_3 + Cl^-$$

While carrying out these general investigations on the reactions of triphenylsilylmethyl compounds we observed that an entirely analogous rearrangement occurred with chloromethyltriphenylsilane and sodium in ethanol

$$Ph_3SiCH_2Cl + Na \xrightarrow{EtOH} \begin{cases} Ph_3SiCH_3 & (34\%) \\ Ph_2Si(R)CH_2Ph & (15\%) \\ (Ph_3SiCH_2)_2 & (14\%) \end{cases}$$

(R = H)

That such a rearrangement had occurred was apparent from the NMR spectrum which showed the characteristic aromatic and aliphatic benzyl absorptions (see Fig. 1). After workup a mixture of rearranged silanol and siloxane products was obtained, these on treatment with alkali in ethanol gave toluene (which was analysed by GLC) together with a mixture of cyclic siloxane $(Ph_2SiO)_4$ and open chain siloxanes. It has been observed previously[27,28] that the eight membered ring rather than the six membered ring compound is generally formed under alkaline conditions.

It was assumed that this rearrangement like those observed previously in this medium was promoted by nucleophilic participation at silicon. The previous workers refluxed for two days and we used similar conditions.

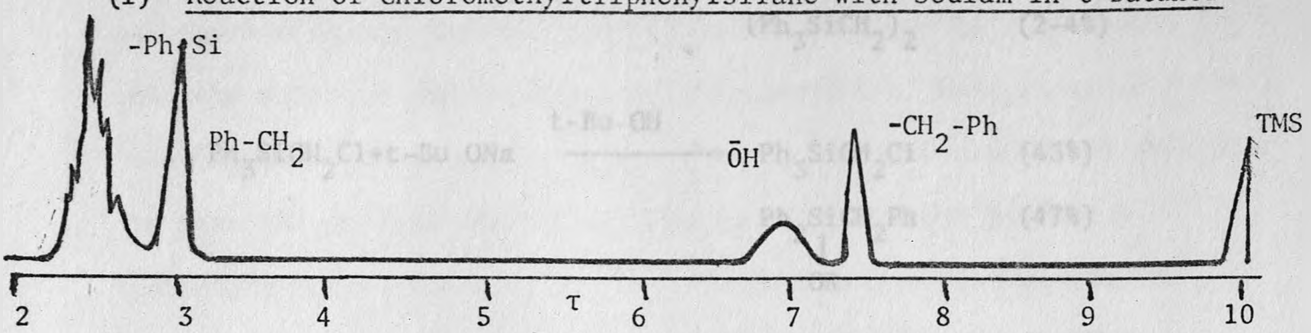
We subsequently observed that this reaction occurred mainly during the period when the metal was dissolving in alcohol and that no reaction occurred with preformed sodium ethoxide under similar conditions.

We also found that higher yields of rearranged product were obtained with sodium in t-butanol or sodium t-butoxide in t-butanol.

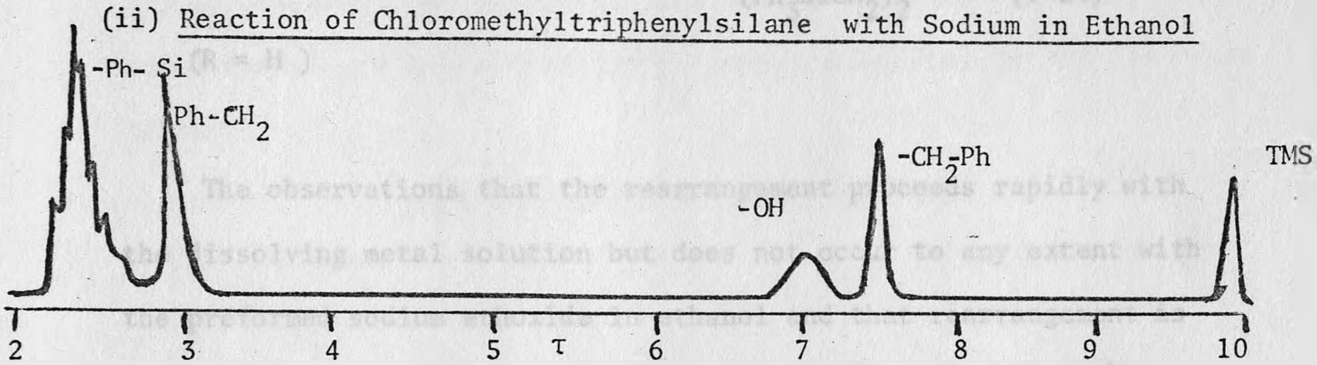
FIG. 1

NMR Spectra of Rearrangement of Chloromethyltriphenylsilane

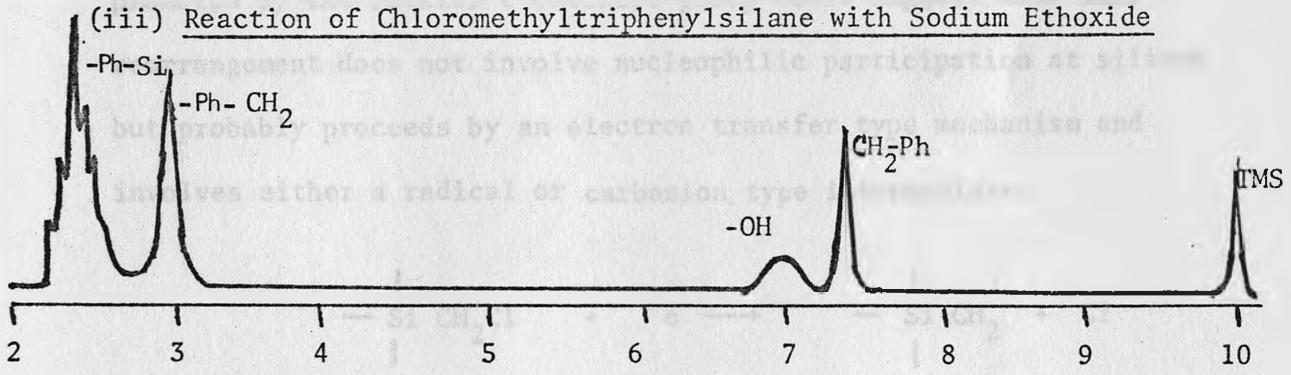
(i) Reaction of Chloromethyltriphenylsilane with Sodium in t-Butanol



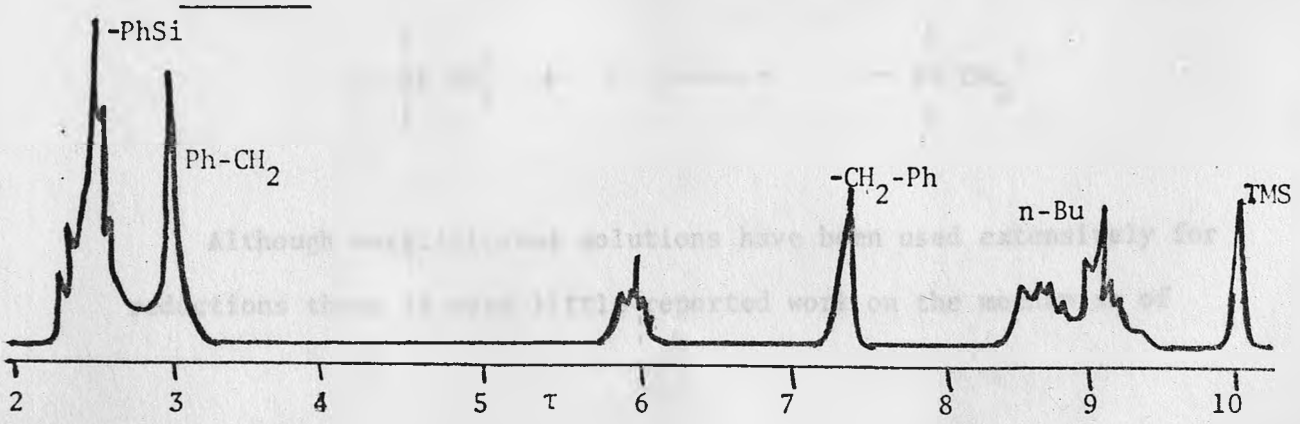
(ii) Reaction of Chloromethyltriphenylsilane with Sodium in Ethanol



(iii) Reaction of Chloromethyltriphenylsilane with Sodium Ethoxide



(iv) Reaction of Chloromethyltriphenylsilane with n-Butyllithium and Silver Chloride



$$Ph_3SiCH_2Cl + Na \xrightarrow{t\text{-}Bu\text{-}OH} \begin{cases} Ph_3SiCH_3 & (35\text{-}60\%) \\ Ph_2Si(OR)CH_2Ph & (20\text{-}32\%) \\ (Ph_3SiCH_2)_2 & (2\text{-}4\%) \end{cases}$$

$$Ph_3SiCH_2Cl + t\text{-}Bu\ ONa \xrightarrow{t\text{-}Bu\text{-}OH} \begin{cases} Ph_3SiCH_2Cl & (43\%) \\ Ph_2Si(OR)CH_2Ph & (47\%) \\ (Ph_3SiCH_2)_2 & (1\text{-}2\%) \end{cases}$$

(R = H)

The observations that the rearrangement proceeds rapidly with the dissolving metal solution but does not occur to any extent with the preformed sodium ethoxide in ethanol and that rearrangement is promoted by the bulkier t-butoxide group would suggest that this rearrangement does not involve nucleophilic participation at silicon but probably proceeds by an electron transfer type mechanism and involves either a radical or carbanion type intermediate.

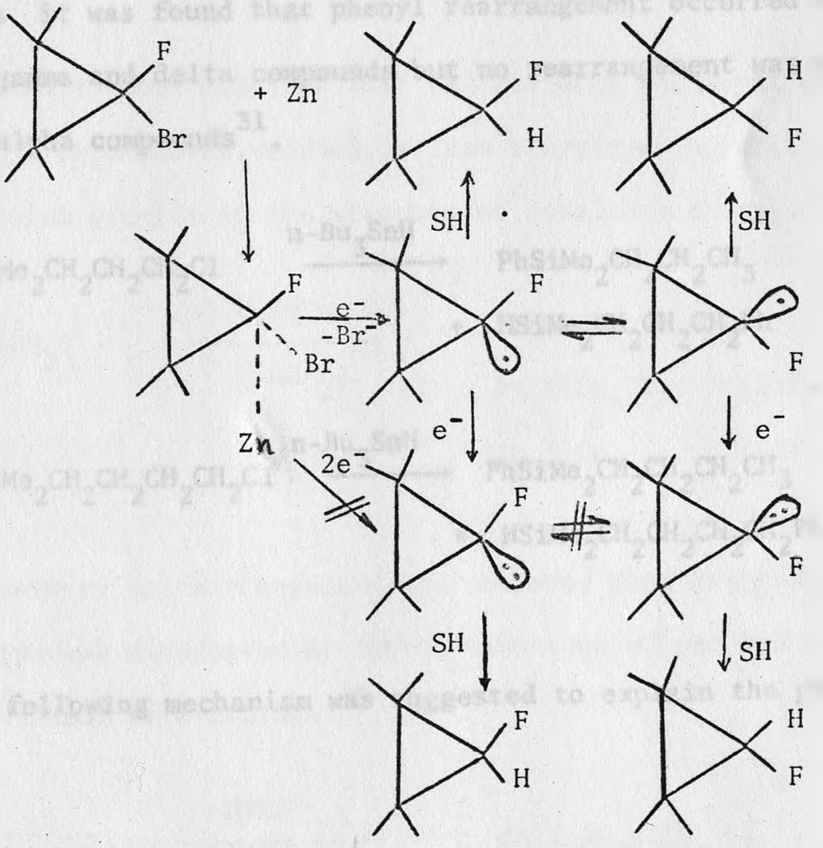
$$-\overset{|}{\underset{|}{Si}}-CH_2Cl + e \longrightarrow -\overset{|}{\underset{|}{Si}}-\overset{\cdot}{C}H_2 + Cl^-$$

$$-\overset{|}{\underset{|}{Si}}-\overset{\cdot}{C}H_2 + e \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2^-$$

Although metal/alcohol solutions have been used extensively for reductions there is very little reported work on the mechanism of

reaction of alkyl halides in such media[29]. Two mechanisms have been proposed for the reactions of gem-dihalocyclopropanes with zinc in alcohol. One is the displacement of halogen as an anion by a two-electron transfer process leading to the formation of a carbanion and the other is the one electron displacement of halogen as an anion leading to a carbon radical which then either reacts with the solvent to form the reduced product or adds another electron to form a carbanion intermediate. As the result of stereochemical studies it was concluded that the most plausible mechanism for the zinc reduction of gem-bromofluorocyclopropanes is as shown in the following scheme.

gem-Dihalocyclopropanes with Zinc



retention inversion

Pyramidal cyclopropyl radicals are formed first by a one-electron transfer; the rate of their inversion is so slow at low temperatures that nearly all of them are converted to cyclopropyl anions by another one-electron transfer and then protonated rapidly to form the stereo-specific reduction product.

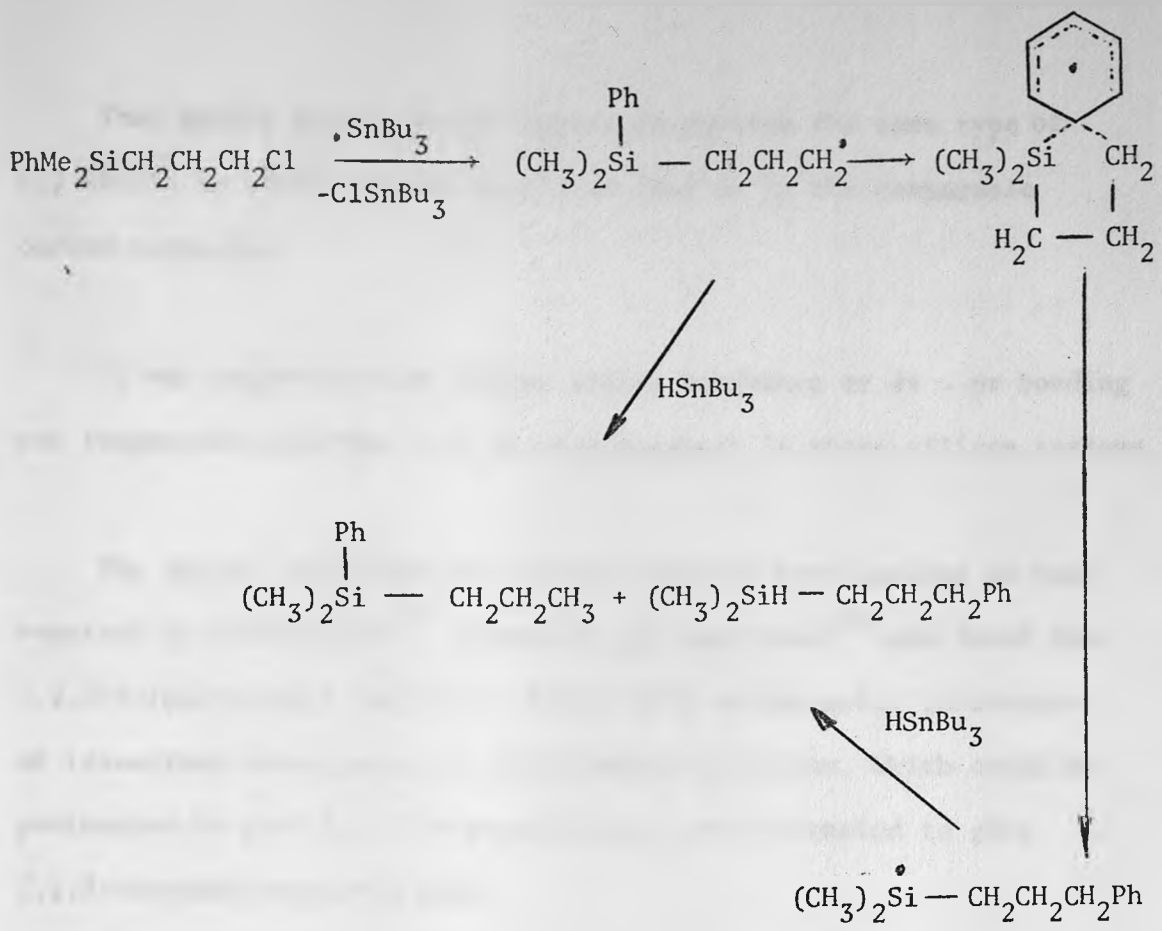
Previous observations would suggest that it is likely that the present reaction also proceeds by a carbanion rather than radical intermediate.

Wilt and his co-workers[30,31] investigated the reactions of alpha, gamma, and delta-halogenoalkylsilanes with n-butyltinhydride in the presence of di-t-butyl peroxide, under these typical radical conditions it was found that phenyl rearrangement occurred readily with the gamma and delta compounds but no rearrangement was observed with the alpha compounds[31].

$$PhSiMe_2CH_2CH_2CH_2Cl \xrightarrow{n\text{-}Bu_3SnH} PhSiMe_2CH_2CH_2CH_3 + HSiMe_2CH_2CH_2CH_2Ph$$

$$PhSiMe_2CH_2CH_2CH_2CH_2Cl \xrightarrow{n\text{-}Bu_3SnH} PhSiMe_2CH_2CH_2CH_2CH_3 + HSiMe_2CH_2CH_2CH_2CH_2Ph$$

The following mechanism was suggested to explain the products[31].



The same workers observed that neither does the alpha compound (Ph_3SiCH_2Cl) chloromethyltriphenylsilane rearrange in reaction with ethylmagnesium bromide in the presence of cobaltous chloride[30].

$$Ph_3SiCH_2Cl \xrightarrow[(CoCl_2)]{EtMgBr} \begin{array}{ll} Ph_3SiCH_3 & (23\%) \\ Ph_3SiCH_2Cl & (31\%) \\ (Ph_3SiCH_2)_2 & (72\%) \end{array}$$

Furthermore no rearrangement was observed when triphenylsilyl-acetaldehyde was decomposed at 150°C, this type of process invariably produces radical intermediates[30].

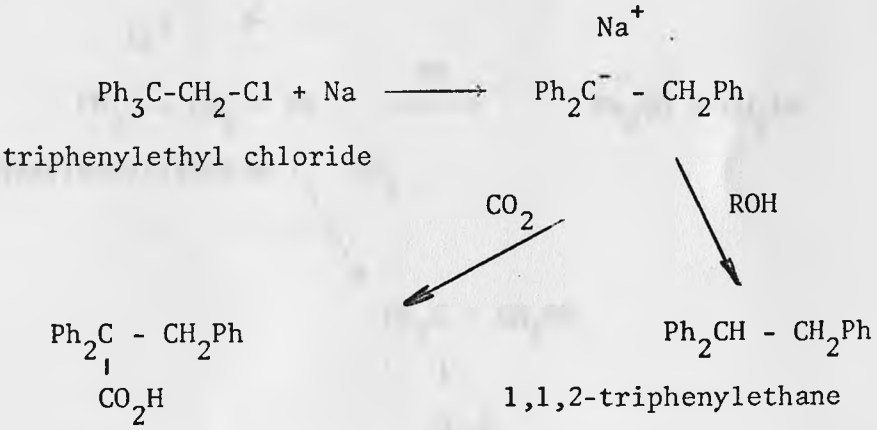
$$Ph_3SiCH_2CHO \xrightarrow[150°]{DTBP} CO + Ph_3SiCH_3 \quad (\text{no } Ph_2SiHCH_2Ph)$$

(DTBP = di-t-butyl peroxide)

Thus phenyl groups do not appear to undergo the same type of 1,2 shifts in silyl alkyl-radicals as they do in the comparable carbon compounds.

It was suggested that either steric hindrance or $d\pi - p\pi$ bonding was responsible for the lack of rearrangement in these silicon systems.

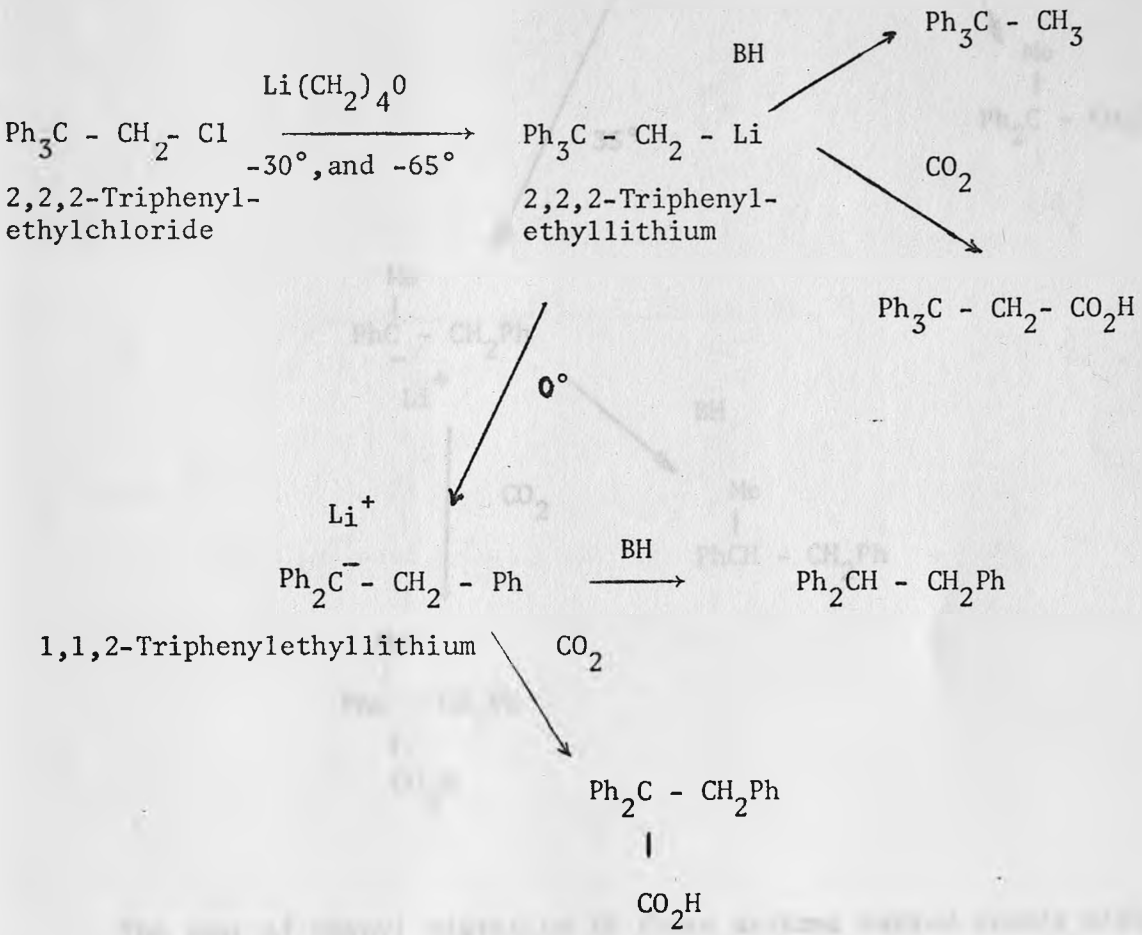
The actual rearrangement obtained appears very similar to that reported by Grovenstein[32], Zimmerman and Smentowski[33] who found that 2,2,2-triphenylethyl chloride treated with sodium metal in dioxane or iso-octane-ether gave 1,1,2-triphenylethylsodium, which could be protonated to give 1,1,2-triphenylethane, or carbonated to give 2,2,3-triphenylpropanoic acid.

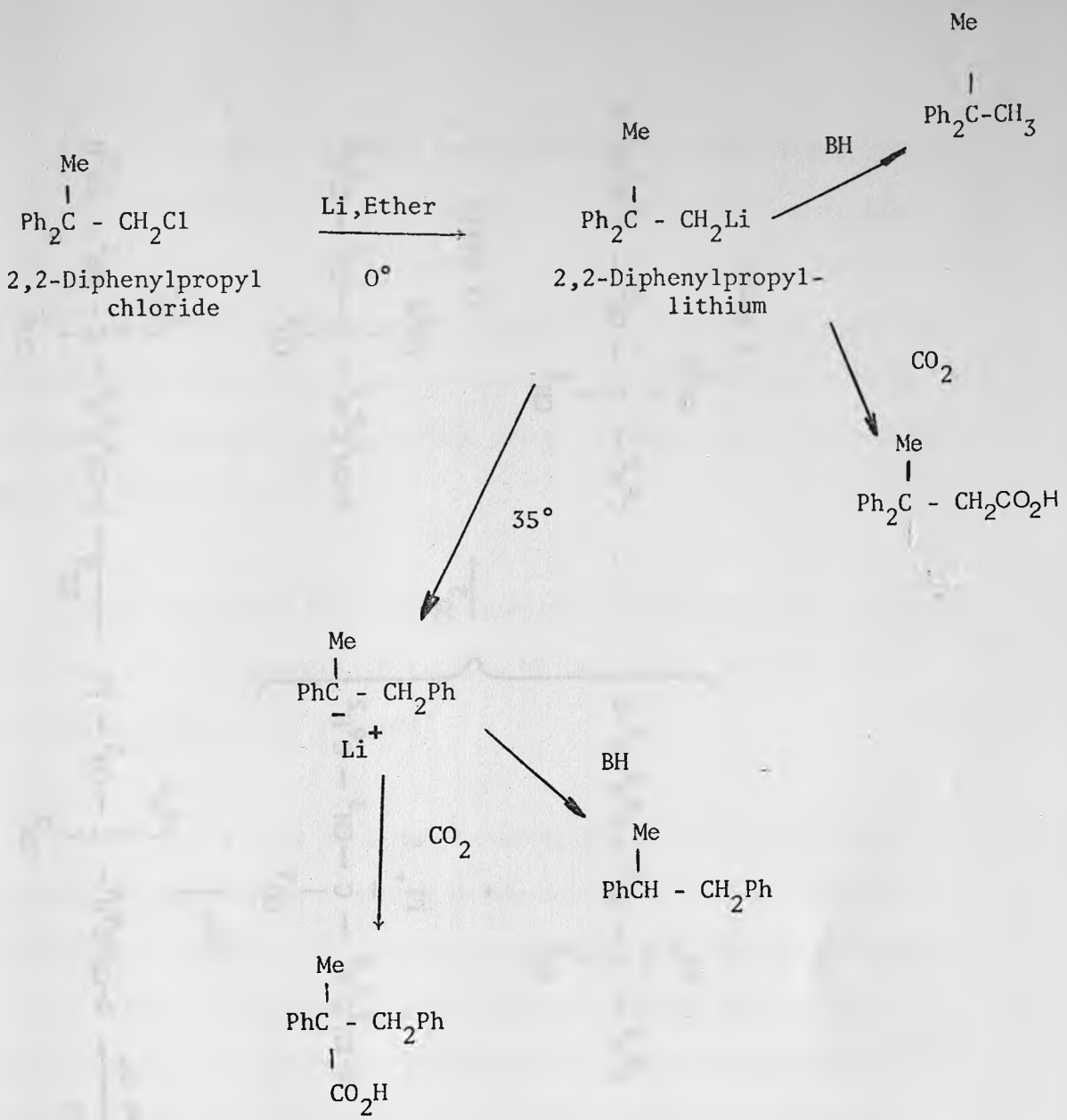


2,2,3-triphenylpropanoic acid.

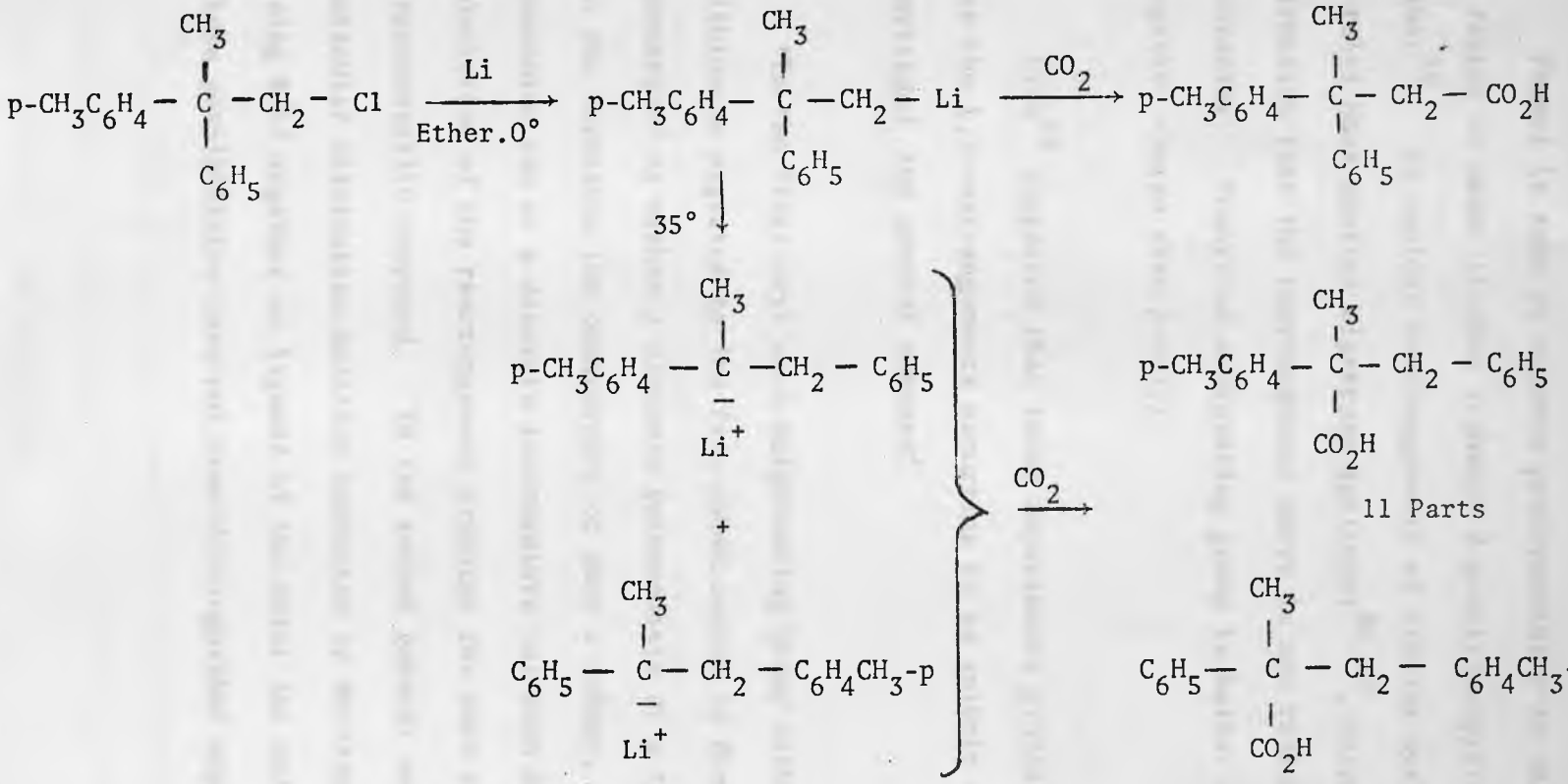
Later studies showed[34,35] that if lithium was substituted for sodium there was no rearrangement at low temperatures but the rearranged product was obtained at high temperature .

Between -30° and -65°, 2,2,2-triphenylethyllithium in THF was shown to be stable, but rearrangement occurred[34] readily at 0°. Similarly in ether at 0°, 2,2-diphenylpropyllithium was formed, and rearrangement occurred[35] at about 35°.





The ease of phenyl migration in these systems varied widely with the metal used. They[34,35] found that the tendency to rearrange is RK ∿ RNa > RLi > R_2Mg, which is in the decreasing order of the ionic character of the carbon-metal bond. This correlation supports a carbanionic mechanism for the rearrangement.

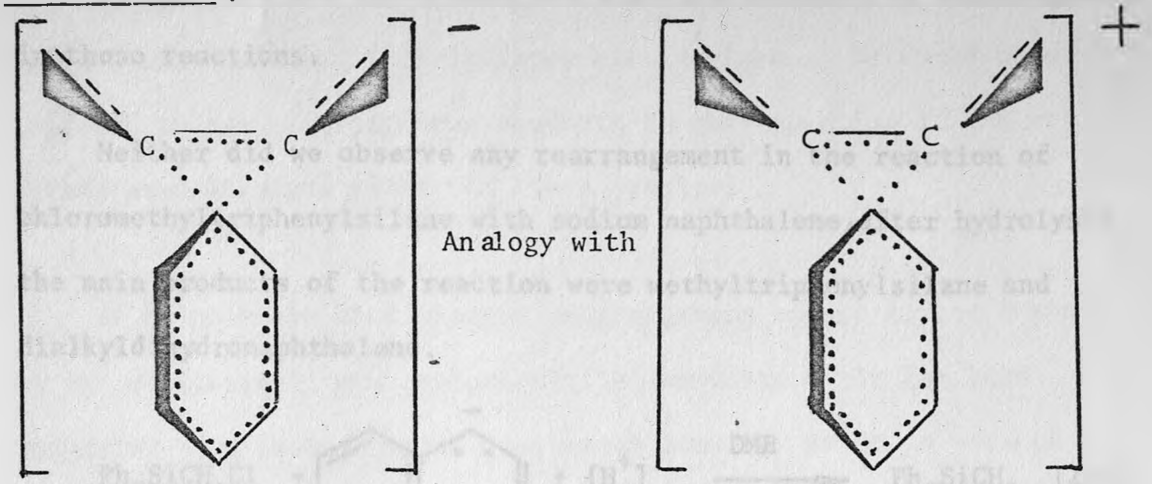

p-CH3C6H4— C(CH3)(C6H5)—CH2— Cl
Li
Ether.0°
p-CH3C6H4— C(CH3)(C6H5)—CH2— Li
CO2
p-CH3C6H4— C(CH3)(C6H5)— CH2— CO2H
35°
p-CH3C6H4 — C(CH3)(Li+) —CH2 — C6H5
+
C6H5 — C(CH3)(Li+) — CH2 — C6H4CH3-p
CO2
p-CH3C6H4 — C(CH3)(CO2H) — CH2 — C6H5
11 Parts
C6H5— C(CH3)(CO2H) — CH2— C6H4CH3-p
1 Part

Phenyl is seen to migrate preferentially to the p-tolyl group by a factor of about 11 when 2-phenyl-2-p-tolylpropyllithium is heated in ether[35]. In radical rearrangements of similar systems phenyl and p-tolyl have similar migratory aptitudes[36,37], which is further confirmation that the rearrangement above is not radical but anionic in character. Phenyl as a migrating group is better able to stabilize negative charge than p-tolyl.

Cram[38] suggested that these experiments provide strong support for the 1,2-rearrangements occurring by an anionic mechanism and envisaged two general schemes:

"In the first aryl as a neighbouring group either dislodges lithium or migrates to the free anionic centre to form an "ethylene phenanion" as either a discrete intermediate or a transition state. In the carbonium ion counterpart of such a scheme, an ethylene phenonium ion as a discrete intermediate has been demonstrated[39,40]. Completion of the rearrangement produces the more stable benzyl organometallic compound. In the second general mechanism, an intramolecular elimination-addition mechanism is envisaged the components being held together as ligands of the metal ion and by ion pairing. These possibilities have not been distinguished experimentally."

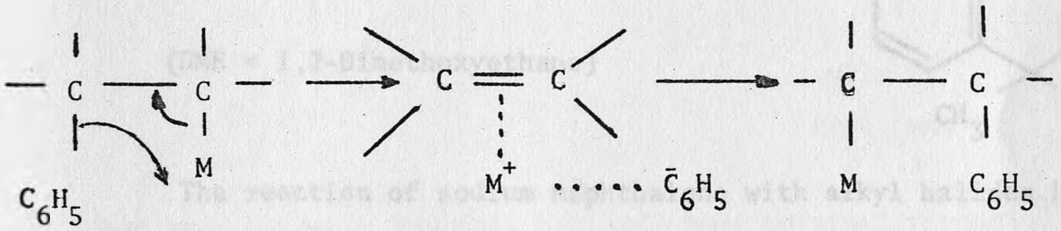
1st Mechanism :



Phenanion as either intermediate or transition state

Phenonium ion, demonstrated to be a discrete intermediate [39]

2nd Mechanism :



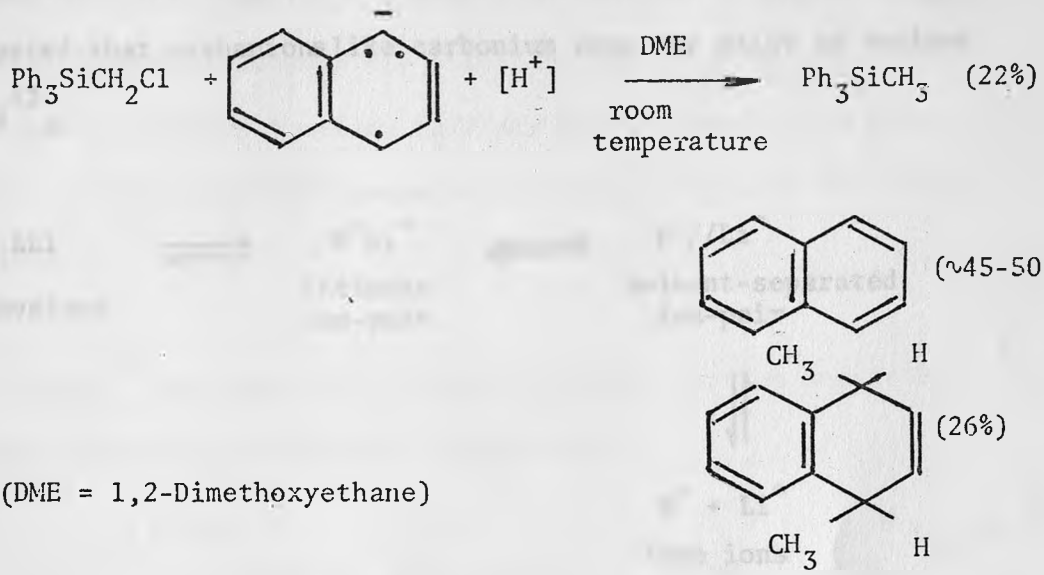
Ion pair with olefin as ligand of the cation.

However, Brook[3] makes no mention of this type of rearrangement in his study of the halogen-metal exchange reactions of halomethyl-triphenylsilyl-derivatives which might be expected to involve carbanion type intermediates.

$$Ph_3SiCH_2X + nBuLi \longrightarrow Ph_3SiCH_2Li + nBuX$$

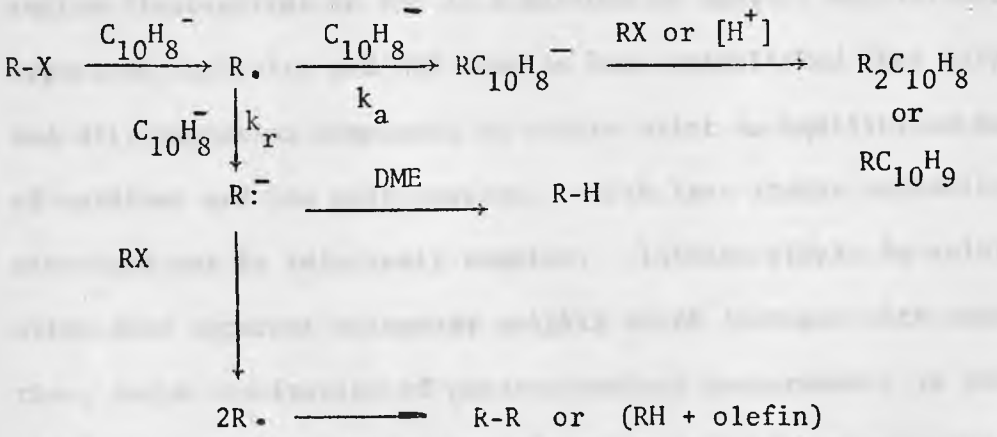
We repeated the Brook work and likewise observed no rearrangement in these reactions.

Neither did we observe any rearrangement in the reaction of chloromethyltriphenylsilane with sodium naphthalene, after hydrolysis, the main products of the reaction were methyltriphenylsilane and dialkyldihydronaphthalene.



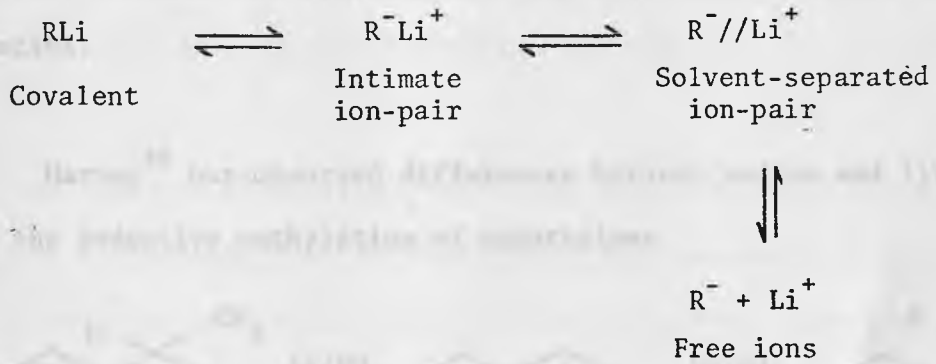
(DME = 1,2-Dimethoxyethane)

The reaction of sodium naphthalene with alkyl halides has been investigated by a number of workers and the following mechanism has been proposed by Garst[41].



A stepwise electron transfer mechanism is suggested and both radical and carbanion intermediates are involved. We would have expected to see rearrangement products in this reaction if the rearrangement involved either of these species.

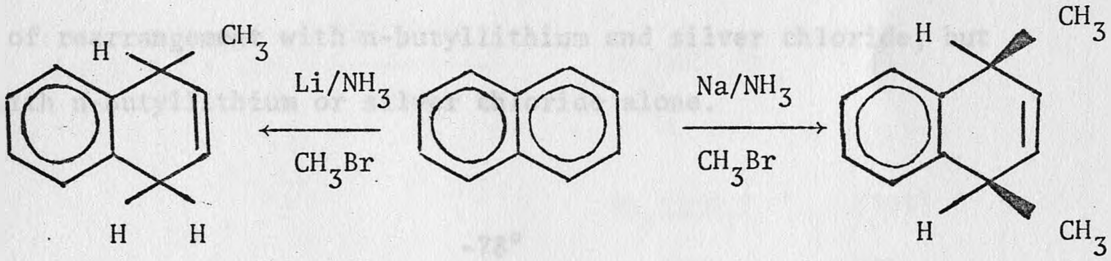
It is possible that whether rearrangement occurs or not depends on the structure of the carbanionic intermediate. It has been suggested that carbanions like carbonium ions may exist in various forms[42],



but good evidence for this has only been obtained recently[43]. Smid and co-workers using UV and conductance methods have shown that sodium fluorenylide in THF is a mixture of contact and solvent separated ion pairs and NMR studies have established that allyllithium and allylmagnesium compounds in ethers exist as equilibrium mixtures of covalent and ion pair species. With less stable carbanions, the structure may be relatively complex. Lithium alkyls in solution often show apparent molecular weights which increase with concentration, and a combination of physicochemical measurements in solution and X-ray structure determination in the solid state suggests that

the structure of these aggregated species varies with the nature of the alkyl group. It is known that Me_3SiCH_2Li trimethylsilylmethyllithium exists as an aggregate in ether solution but the structure of Ph_3SiCH_2Li triphenylsilylmethyllithium in ether solution has not been determined. However the factors which determine whether a given organometallic compound exists as an aggregate, a covalent monomer, or as ion-pairs in solution may be fairly finely balanced. $Ph_3SiCH_2^-$ being of intermediate stability may exist as aggregates or covalent monomers in ether solvents but as ions or ion pairs in alcohol solvents and rearrangement may only occur with the ionic species.

Harvey[44] has observed differences between sodium and lithium in the reductive methylation of naphthalene.



Harvey[44] suggests the observed metal effect is explicable as a consequence of : (1) the greater tendency of lithium than sodium to form solvent-separated rather than contact ion pairs in solution[45]; and (2) more facile protonation of the former by the medium[46]. In this hypothesis, the monolithio anion ($Li^+//\bar{N}CH_3$) formed on initial alkylation of the dilithio dianion[47] ($2Li^+$, $N^=$) is solvent-separated and susceptible to protonation by ammonia to form I (eg.2), whereas the corresponding monosodio anion exists as an intimate ion pair

(Na^+, $\bar{N}CH_3$) able to persist in the medium sufficiently long to undergo a second alkylation, leading to formation of II (eg.1).

$$2M^+, N^= \xrightarrow{RX} M^+,\bar{N}R \xrightarrow{RX} NR_2 + MX \qquad \text{(eg.1)}$$

II

$$MX + M^+//\bar{N}R \xrightarrow{NH_3} HNR + MNH_2 \qquad \text{(eg.2)}$$

I

M^+ = Na, Li; N = naphthalene; R = CH_3

We also considered the possibility that these rearrangements may occur via carbene type intermediates since we observed the same type of rearrangement with n-butyllithium and silver chloride, but not with n-butyllithium or silver chloride alone.

$$Ph_3SiCH_2Cl + nBuLi + AgCl \xrightarrow[THF:Et_2O:hexane = 4:1:1]{-78^\circ} \begin{cases} (Ph_3SiCH_2)_2 & (6\%) \\ Ph_3SiCH_2Cl & (38\%) \\ Ph_2SiCH_2Ph \\ \quad | \\ \quad nBu & (8\%) \end{cases}$$

The reactions of chloromethyltriphenylsilane with n-butyllithium and silver chloride and with sodium ethoxide in ethanol were carried out in the presence of cyclohexene but no cyclopropane type products were detected.

A closely analogous rearrangement to that reported here involves a hydride ion shift from silicon to carbon. It occurs along with Si - H solvolysis when dimethylsilylmethyl chloride or iodide is treated with potassium hydroxide in aqueous ethanol[48] eg.

$$HO^- + HMe_2SiCH_2I \longrightarrow HOMe_2SiCH_3 \quad (89\%) + I^-$$

$$HO^- + H_2O + HMe_2SiCH_2I \longrightarrow H_2(11\%) + HOSiMe_2CH_2I + HO$$

We found the iodomethyltriphenylsilane (Ph_3SiCH_2I) likewise underwent rearrangement in this medium.

$$Ph_3SiCH_2I + KOH \xrightarrow[1\ hour]{95\%\ EtOH} \begin{cases} Ph_2\underset{R}{Si}CH_2Ph & (25\%) \\ Ph_3SiCH_2I & (70\%) \\ Ph_3SiOH & (5\%) \end{cases}$$

In contrast chloromethyltriphenylsilane shows no reaction under the conditions used for the iodide. It does react if refluxed for several days but then the only detectable product is triphenylsilanol.

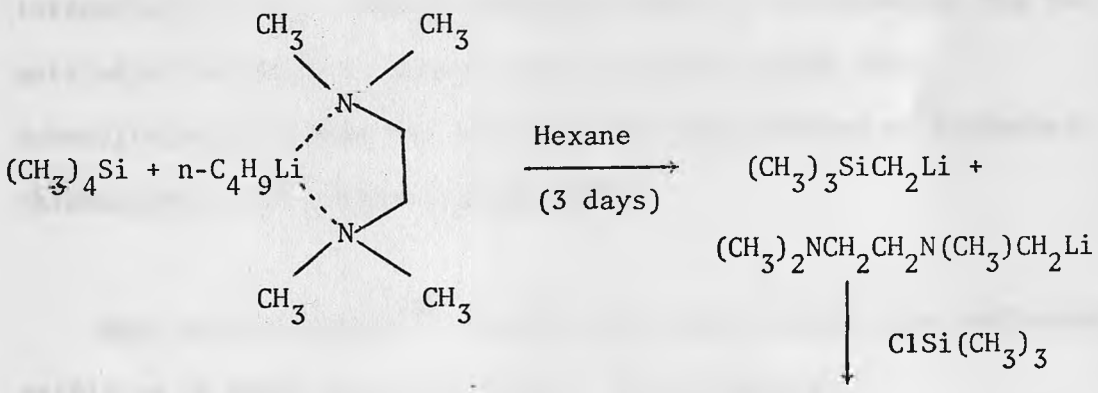
The ready rearrangement of the iodide in potassium hydroxide aqueous ethanol may be due to nucleophilic participation or may be due to the higher reactivity of iodides in electron transfer process.

CHAPTER III

METALATION OF [$^2H_3$]-METHYLTRIPHENYLSILANE

I Introduction

Peterson[8] has reported that trimethylsilylmethyllithium is formed from the reaction of tetramethylsilane with n-butyllithium tetramethylethylenediamine (n-butyllithium. TMEDA) in 36% of yield after 3 days. The methylsilanes appear to be only slightly more reactive in metalation reactions than methylamines as evidenced by the detection of $(CH_3)_2NCH_2CH_2N(CH_3)CH_2Li$ in approximately 18% yield in the same reaction.



$$[(CH_3)_3Si]_2CH_2 \quad + \quad (CH_3)_2NCH_2CH_2N(CH_3)CH_2Si(CH_3)_3$$
$$(36\%) \qquad\qquad (18\%)$$

Gornowicz and West[9] have shown that a wide variety of trimethylsilyl derivatives (Me_3SiX, where X = chloro, methoxy, ethoxy, trimethylsiloxy) undergo extensive methyl-lithiation even though the substituents are known to be readily displaceable by nucleophiles.

$$(CH_3)_3SiX + \text{t-BuLi. TMEDA} \xrightarrow{THF} LiCH_2Si(CH_3)_2X + (CH_3)_3Si - \text{t-Bu}$$

Trimethylchlorosilane also reacts with tertiary-butyl-lithium, tetramethylethylenediamine, (t-butyl-lithium, TMEDA) in pentane exothermically to give, within less than 1 minute at room temperature 60% methyl metalation and 20% coupling[9],

$$(CH_3)_3SiCl + \text{t-BuLi. TMEDA} \longrightarrow LiCH_2Si(CH_3)_2Cl \quad (\sim 60\%) + (CH_3)_3Si\text{-t-Bu} \quad (\sim 20\%)$$

under these conditions the metalation of tetramethylsilane afforded only 40% metalation during 4 days, which suggest that the protons in trimethylchlorosilane are significantly more acidic than those in tetramethylsilane. Steric hindrance seems to be essential for the metalation reaction to compete with coupling, since only n-butyltrimethylsilane was obtained from the reaction of trimethyl-chlorosilane with n-butyllithium.TMEDA[9].

Bush and co-workers[49] reported that silyl-amines are sufficiently acidic to be metalated by N-lithio- N-silylamines,

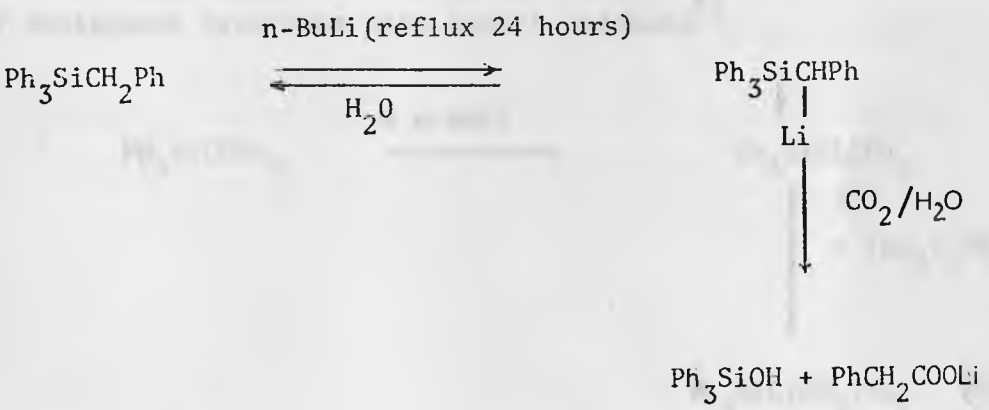
$$(CH_3)_3SiNLi\text{-t-Bu} + (CH_3)_3SiN(CH_3)_2 \longrightarrow (CH_3)_2NSi(CH_3)_2CH_2Li + (CH_3)_3SiNHt\text{-Bu}.$$

and it has been observed that tetramethylsilane may even undergo polylithiation with t-butyl-lithium in THF[50].

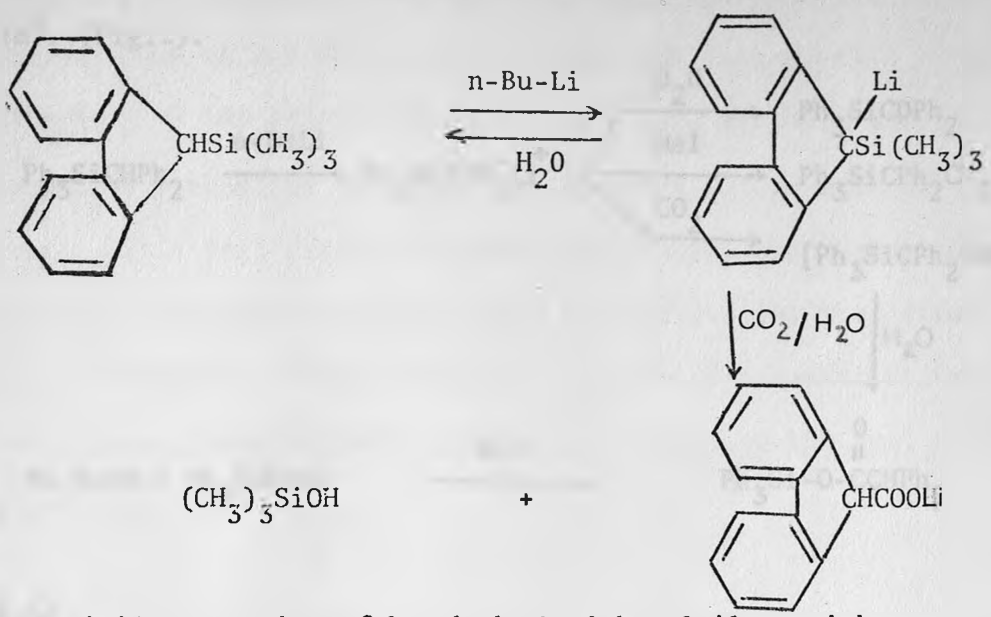
$$(CH_3)_4Si + \text{t-BuLi} \xrightarrow{THF} \xrightarrow{D_2O} \text{poly-deuteriated TMS.}$$

Brook[3] stated that neither methyltriphenylsilane nor bis(triphenylsilyl)methane could be metalated to any appreciable extent with n-butyllithium TMEDA.

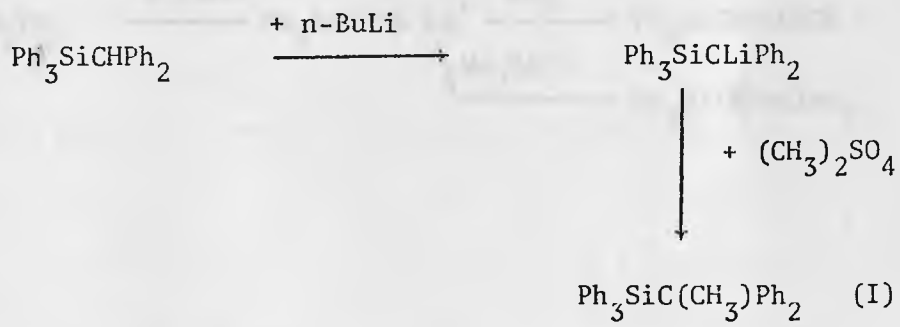
Although it is possible to metalate a methyl group to which one or more phenyl groups is directly attached, Gilman and co-workers have shown that benzyltriphenylsilane[51], benzhydryltriphenylsilane[52] and 9-fluorenyltrimethylsilane[53] undergo the metalation reaction. When triphenylbenzylsilane was treated with an excess of n-butyllithium, the carbonation of the reaction mixture gave triphenylsilanol and phenylacetic acid. The acid formed is quite unstable, resulting in cleavage of a carbon to silicon bond[51].



Hydrolysis of this reaction gave a good yield of starting material, indicating that the initial reaction is a metalation[51]. This was similar to thereaction of 9-fluorenyltrimethylsilane with n-butyllithium[53].

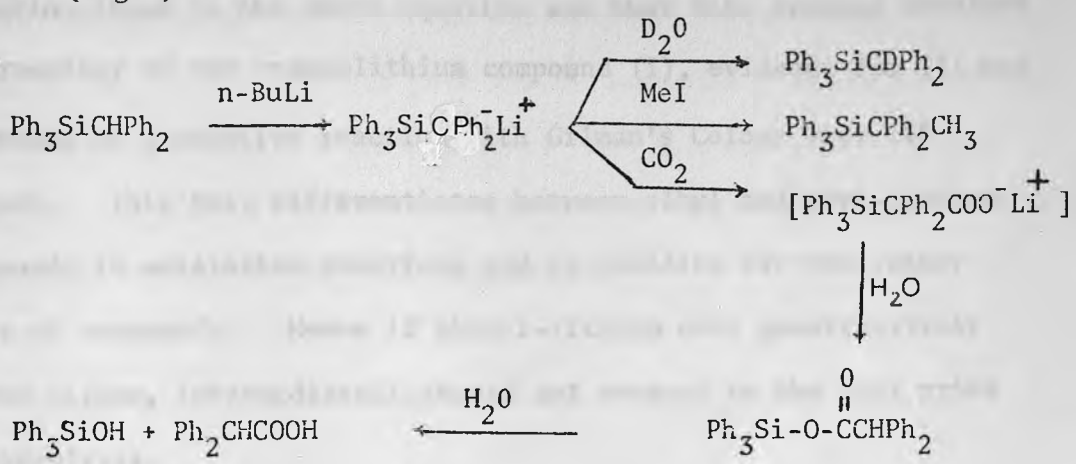


A similar reaction of benzhydryltriphenylsilane with n-butyllithium in a mixture of THF and ether gave (I) in 58% yield after subsequent treatment with methyl sulphate[52].

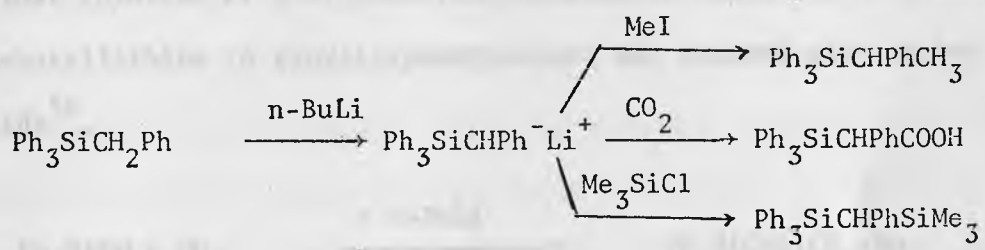


Brook's re-investigation[3] showed that virtually quantitative metalation of benzhydryltriphenylsilane could be effected at room temperature using n-butyllithium in THF and the resulting organometallic was deuteriated or methylated in greater than 80% yield. Carbonation to give the expected triphenylsilyldiphenylacetic acid gave only a mixture of diphenylacetoxytriphenylsilane, triphenylsilanol, and diphenylacetic acid. These products were those expected from the base-catalized rearrangement of triphenylsilyldiphenylacetic acid, a reaction which has been shown to occur readily with silylacetic

acids under mild conditions[77] (Fig.1). Metalation of benzyltriphenylsilane using n-butyllithium in ether gave the lithium reagent in good yield[3]. (Fig.2).

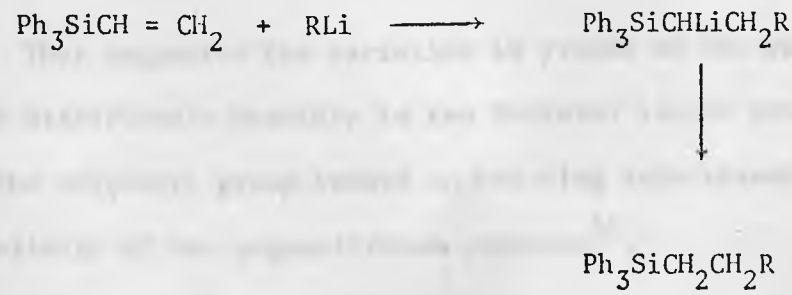


(Fig.1)



(Fig.2)

Cason and Brooks[54,55] have shown that a variety of organolithium reagents add to the double bond of vinyltriphenylsilane to give substituted 1-triphenylsilylethyllithium derivatives[54,55].



and they established that the organolithium compound added in the direction shown in the above equation and that this process involved intermediacy of the organolithium compound (I), evidence for (I) was indicated by a negative reaction with Gilman's Colour Test III reagent. This test differentiates between alkyl and aryl-lithium compounds in metalation reactions and is positive for the latter class of compounds. Hence if phenyl-lithium adds quantitatively to the silane, intermediate(I)should not respond to the test prior to hydrolysis.

Also a low yield of α-triphenylsilylheptanoic acid resulted when an ether solution of 1-triphenylsilyl-n-hexyllithium from the addition of n-butyllithium to vinyltriphenylsilane was treated with carbon dioxide[55].

$$Ph_3SiCH = CH_2 \xrightarrow{+\ n\text{-BuLi}} Ph_3SiCHLiCH_2\text{-}Bu \xrightarrow[2.H_2O]{1.CO_2} Ph_3SiCH(COOH)\text{-}CH_2Bu$$

They suggested the variation in yields of the addition products were attributable possibly to two factors: steric interference offered by the triphenyl group toward an entering substituent and the relative reactivity of the organolithium compound[55].

Subsequently Brook[3] found that the addition of phenyllithium to vinyltriphenylsilanes in ether was complete in less than 16 hours. Deuterolysis of the reaction gave 78% of deuterium labelled 1-phenyl-2-triphenylsilylethane ($Ph_3SiCHDCH_2Ph$)[3] and Mulvaney and Gardlund reported that 25% of t-$BuCH_2CHLiSi(CH_3)_3$ was obtained from the addition of t-butyl-lithium to vinyltrimethylsilane[56].

$$t\text{-BuLi} + (CH_3)_3SiCH = CH_2 \xrightarrow[-40°]{Et_2O} (CH_3)_3SiCHLiCH_2\text{-t-Bu} \quad (25\%)$$

Organolithium compounds are known to undergo addition to the carbon-carbon double bonds of highly conjugated molecules like 1,1-diphenyl-ethylene and the fulvenes and to simple conjugated dienes in the initiation of polymerisation[57], but the addition of alkyl and aryl-lithium compounds to comparatively simple olefins is a relatively rare phenomenon. It has been suggested that these reactions occur because silicon with its vacant d-orbitals can stabilise an adjacent negative charge, this has also been suggested to explain the ready metalation of the alkylsilicon compounds. It would be expected that electronegative substituents on silicon promote these reactions and as described above Gornowicz and West[9] found that the Me_3SiX (X = chloro, methoxy, ethoxy,trimethylsiloxy) underwent metalation more rapidly than Me_4Si. Similarly the inductive effect of the phenyl group is apparent in the reaction of $R_3SiCH = CH_2$ compounds with organolithium compounds. The triphenyl derivatives reacted rapidly whereas the trimethyl-compounds react slowly. It is therefore

very surprising that no metalation was observed in the reaction of methyltriphenylsilane with n-butyllithium TMEDA. Our feeling was that metalation must occur but that the organometallic intermediate must react so readily with the medium that it was undetectable. To prove this point we decided to prepare [$^2H_3$]-methyltriphenylsilane (Ph_3SiCD_3) and study its exchange reaction. The route chosen for the preparation of Ph_3SiCD_3 was the following

$$Ph_2SiCl_2 + PhLi \longrightarrow Ph_3SiCl$$

$$Ph_3SiCl + CD_3MgI \longrightarrow Ph_3SiCD_3$$

Fully deuteriated methyliodide is a common starting material in the preparation of compounds containing [$^2H_3$] methyl group. The usual method of preparing deuteriated methyl iodide involves deuteriation of malonic acid $CH_2(CO_2H)_2$ followed by decarboxylation to yield [$^2H_3$] acetic acid (CD_3CO_2H) then conversion of this into the silver salt and finally decarboxylation by heating with iodine. This method involves a number of steps and gives very poor yields. A more convenient method of preparing deuteriated methyl iodide CD_3I yielding also deuteriated dimethylsulphoxide, [$^2H_6$] dimethyl sulphoxide was suggested by Kunn and Trischmann[58], that trimethyl-sulphoxonium iodide $(CH_3)_3SOI$ made by the addition of methyl iodide to dimethyl sulphoxide $(CH_3)_2SO$, could be pyrolysed smoothly back to these substances.

$$(CH_3)_2SO + CH_3I \longrightarrow (CH_3)_3S^+OI^-$$

$$(CH_3)_3S^+OI^- + D_2O \text{ (excess)} \longrightarrow (CD_3)_3S^+OI^- + H_2O$$

$$(CD_3)_3S^+OI^- \xrightarrow{\text{Pyrolysis}} CD_3I + (CD_3)_2SO$$

$$CD_3I + Mg \longrightarrow CD_3MgI$$

II The Reaction of [$^2H_3$]-Methyltriphenylsilane with t-Butyl-lithium

In order to investigate the possibility of the metalation of [$^2H_3$]-methyltriphenylsilane, Ph_3SiCD_3, thereaction of [$^2H_3$]-methyltriphenylsilane with t-butyl-lithium in THF at -78° for 2 hours was performed under standard conditions. The starting material [$^2H_3$]-methyltriphenylsilane was the only product obtained.

$$Ph_3SiCD_3 + \text{t-BuLi} \xrightarrow[-78^\circ]{\text{THF (2 hours)}} \xrightarrow[(H_2O/H^+)]{} Ph_3SiCD_3 \ (95\%)$$

III The Reaction of [$^2H_3$]-Methyltriphenylsilane with n-Butyllithium TMEDA

Because the order of the reacitivities of the organolithium metalating agents appear to be t-butyl-lithium. TMEDA > n-butyllithium. TMEDA > t-butyl-lithium > n-butyllithium and because of the high reactivity of the TMEDA-complexed organolithium compounds toward R_3SiCH_3[59], we decided to carry out the reaction of [$^2H_3$]-methyltriphenyl-silane with n.-butyllithium TMEDA in THF at room temperature for 18 hours. The coupling product, Ph_3SiCD_2-Bu (30%) and starting material Ph_3SiCD_3 (70%) were obtained.

$$Ph_3SiCD_3 + \text{n-BuLi.TMEDA} \xrightarrow{\text{THF}} \xrightarrow{(H_2O/H^+)} \begin{matrix} Ph_3SiCD_3 \ (70\%) \\ Ph_3SiCD_2Bu \ (30\%) \end{matrix}$$

IV The Reaction of [$^2H_3$]-Methyltriphenylsilane with t-Butyl-lithium. TMEDA

The reaction of [$^2H_3$]-methyltriphenylsilane with t-butyl-lithium. TMEDA in THF at room temperature for 18 hours gave the exchange product Ph_3SiCD_2H (5-10%), the coupling product Ph_3SiCD_2-tBu (10%) and starting material Ph_3SiCD_3 (80%).

$$Ph_3SiCD_3 + \text{t-BuLi TMEDA} \xrightarrow[18\text{ hours}]{\text{THF}} \xrightarrow{H_2O/H^+} Ph_3SiCD_2H \quad (5\text{-}10\%)$$
$$+ Ph_3SiCD_2\text{-t-Bu} \quad (10\%)$$
$$+ Ph_3SiCD_3 \quad (80\%)$$

The relative proportions of Ph_3SiCD_2H and Ph_3SiCD_3 compounds was confirmed and determined from the intensities of the M^+ ions at 276 and 277.

The observation of this exchange in the [$^2H_3$]-methyltriphenylsilane confirms our belief that metal exchange does take place with methyltriphenylsilane but is not observed due to rapid reaction with the medium. The observed exchange in the deuteriated system is relatively small (5-10%) however it is possible that considerable exchange could take place in the light methyltriphenylsilane. Studies of carbanion forming reactions report [78, 79] isotope effects $k_H/k_D \simeq 5$ for such systems, so the extent of exchange in the light system under our conditions could be of the order of 50%.

EXPERIMENTAL

All melting points and boiling points are uncorrected, and all experiments involving organometallic compounds were carried out in an atmosphere of purified nitrogen.

NMR spectra were usually determined at 35° (unless otherwise stated). Routine spectra were recorded at 60 MHz , using either a Varian Associates A-60A spectrometer or a Perkin-Elmer R-10 model. For the accurate integration of dilute solutions (10% w/v or less), spectra were recorded at 100 MHz/sec with a Perkin-Elmer R-14 spectrometer. Unless otherwise stated, spectra were recorded from samples of neat liquids or 20% solutions in carbon tetrachloride or deuterochloroform. Absorption positions are quoted relative to tetramethylsilane (τ 10.00) as internal standard. Spectral assignments were based on the data of Mathieson[60].

IR spectra were obtained using a Perkin-Elmer Infracord 237 and the interpretation of absorption bands was based on the texts of Bellamy[61] and Flett[62]. The anticipated silicon-methyl or silicon-phenyl absorptions were observed in all compounds and are not individually recorded.

GLC analyses were carried out on a Pye-Unicam series 104 instrument using a silicone gum SE 30 column (9ft. x 1/8 in. o.d. or 5ft.x 1/8 in.o.d.) with helium as a carrier gas at a flow rate of 50ml./min. Temperatures for individual separations are recorded in the text.

Mass spectra were determined using an A.E.I. MS9 mass spectrometer. Normal operating conditions consisted of an ionising potential of 70 e.v. and an inlet temperature of 150°C.

TLC was carried out using silica gel (ex Camlab Ltd.) spread to a thickness of 0.25 mm according to the manufacturer's instructions. The 0.25 mm thickness silica coated plastic sheet (no gypsum) were also used for TLC plates, supplied by Macherey-Nagel&CO. The TLC were run at room temperature.

Column Chromatographic Separations were performed on a column (approximately $1\frac{1}{2}$ft. x 1 in. diameter) using 'silica gel M.F.C.'. AnalaR. grade solvents were employed in all chromatographic experiments.

Reagents Organosilanes were kindly donated by Midland Silicones Ltd., and the remaining chemicals were purchased from Messrs. Hopkin and Williams Ltd. or the alternative supplier indicated. The "AnalaR." reagents benzene, light petroleum (60-80°), carbon tetrachloride and diethylether were used without further purification. Organometallic reagents were prepared in reagent grade diethylether or tetrahydrofuran previously redistilled from lithium aluminium hydride. Solvents used for chromatography were redistilled before use.

All alkyl halides were distilled before use.

For the reactions of organometallics, unless otherwise stated, the experiments were performed using 'magnesium turnings for Grignard reaction' having the following batch analysis (%):-

minimum assay - 99.75

zinc	- 0.01	nickel	- 0.001
aluminium	- 0.007	lead	- 0.003
silicon	- 0.007	calcium	- 0.003
copper	- 0.001	cadmium	- 0.0003
manganese	- 0.004	iron	- 0.008
tin	- 0.001	manganese dioxide	- 0.1

The deuterium oxide was supplied by Koch-Light, purity > 99.75% and a fresh ampoule was opened for each experiment.

A. ORGANOMETALLIC REACTION

1. Reaction of (3-Bromopropyl)triphenylsilane with Magnesium

(3-Bromopropyl)trichlorosilane

Chloroplatinic acid (0.001 gm, 0.0000024 mole) in isopropanol (0.1 ml) was added to allyl bromide (34 gm, 0.28 mole) and was refluxed. Trichlorosilane (39 gm, 0.0281 mole) was added to this reaction mixture dropwise for 6 hours and was refluxed for 30 hours. The reaction mixture was distilled and a yield of (3-bromopropyl)trichlorosilane 31 gm (43%) was obtained at bp.80-87°/14. ^{1}H n.m.r. τ 6.5(t,2H,CH_2Br), 7.8(m,2H,CH_2), 8.3(m,2H,CH_2Si).

(3-Bromopropyl)triphenylsilane

Phenyl-lithium (0.3 mole) in anhydrous diethylether (250 ml) was added dropwise to a solution of (3-bromopropyl)trichlorosilane (0.1 mole) in anhydrous ether (20 ml). After addition was complete the reaction mixture was quenched with water, the organic phase separated, the solvent removed, and the residue recrystallised from ethanol, yield 50%, m.p.90-92° (lit.[4], m.p.91-92°); ^{1}H n.m.r. τ 2.37-2.80 (m,15H, aromatic CH) 6.65(t,2H,CH_2Br) 7.84-8.17(m,2H,CH_2) 8.38-8.64(m,2H,CH_2Si).

Reaction of (3-triphenylsilyl)propylmagnesium bromide with

(a) deuterium oxide - A solution of (3-bromopropyl)triphenylsilane (0.0026 mole) in dry diethylether (5 ml) was added dropwise to magnesium (0.01 mole) in dry diethylether (2 ml). After addition was complete the reaction mixture was refluxed for 30 mins, then quenched with excess deuterium oxide. The concentrated organic

phase was chromatographed on silica gel, using light petroleum/ benzene (9:1) as eluant. There was obtained a mixture of propyltriphenylsilane (12%) and 3-d_2-propyltriphenylsilane (60%), m.p. 83-84° (lit.[4] m.p. 84°); ^{1}H n.m.r. τ 2.30-2.83(m,15H, aromatic CH) 8.33-8.87(m,4H,CH_2) 8.87-9.26(m,2.2H,CH_2CH_2Br); relative proportions of the two compounds was estimated from the intensities of the M^+ ions at 302 and 303. Elution with benzene gave 1,6-bis(triphenylsilyl) hexane (22%) m.p.123-125°; ^{1}H n.m.r. τ 2.30-2.87 (m,15H, aromatic CH) 8.65 (s,6H, CH_2).

(b) Carbon dioxide - (3-triphenylsilyl)propylmagnesium bromide was prepared as was prepared above. Dry carbon dioxide was passed over the surface of the reaction mixture for 30 mins. After hydrolysis and concentration the products were chromatographed on silica gel. Elution with light petroleum/ benzene (9:1) gave propyltriphenylsilane (16%), elution with benzene gave 1,6-bis(triphenylsilyl) hexane (24%), elution with diethylether gave (3-carboxypropyl)triphenylsilane (50%) m.p. 171-172° (lit.[4] m.p. 171-172°); ^{1}H n.m.r. τ 2.35-2.95 (m,5H, aromatic CH) 7.75 (t,2H,J7Hz,CH_2CO_2-) 8.10-8.55 (m,2H,CH_2) 8.55-8.90 (m,2H,CH_2-Si) 0.90 (s,1H,OH).

2. Reaction of Halogenomethyltriphenylsilanes with Magnesium

Reagents 'Specpure' magnesium crystals were supplied by Johnson Matthey Chemicals Limited. Magnesium powder was purchased from Fisons Limited.

Bromomethyltriphenylsilane was kindly supplied by Dr.R.J.Rowley[5] and also prepared by using the method of Brook and co-workers[3], m.p. 121-122.5°C(lit.[3],121-122°C), ^{1}H n.m.r. τ 2.30-2.80 (m,15H) and 6.9(s,2H).

Chloromethyltriphenylsilane was prepared using the method of Huang and co-worker[14], m.p. 112-114°C, (lit.[14] 113-114°C) ^{1}H n.m.r. τ 2.30-2.85 (m,15H, aromatic CH) 6.45-6.5 (s,2H, CH_2Cl).

Chloromethyltrichlorosilane was prepared by the method of Jones[64].

Methyltrichlorosilane (1 lit) was contained in the flask with azo-bis-isobutyronitrile (0.1 g). Chlorine (1 ml/sec) was bubbled through and the heating adjusted to ensure a slow reflux (60°C). The chlorination was carried out in the dark for 8 hours and the product isolated by fractional distillation.

Yield was 10% but by recycling and further chlorination a yield of 50% based on starting material was obtained. There was a 2/1 ratio of chloromethyltrichlorosilane to dichloro-methyltrichlorosilane in the product GLC. . B.p. figures: CH_3SiCl_3, 66°C; $(CH_2Cl)SiCl_3$, 119°C; $(CHCl_2)SiCl_3$, 144°C.

2.1 Reaction of Bromomethyltriphenylsilane with Johnson Matthey 'Specpure' Magnesium Crystals

A solution of bromomethyltriphenylsilane (0.0026 mole) in dry diethylether (5 ml) was added dropwise to Johnson Matthey 'specpure' magnesium crystals (0.01 mole) in dry diethylether (2 ml). After addition was complete the reaction mixture was refluxed with stirring for 18 hours. Dry carbon dioxide gas was passed over the surface of the reaction mixture for 30 min. After hydrolysis, the organic phase was dried over magnesium sulphate and after removal of the ether

solvent by evaporation, the yields were methyltriphenylsilane (70%) ^{1}H n.m.r. τ 2.38-2.9(m,15H, aromatic CH), τ 9.2(s,3H,CH_3) and 1,2-bis(triphenylsilyl)ethane (30%) ^{1}H n.m.r τ 2.28-2.9(m,15H, aromatic CH), τ 8.78-8.8(s,4H,$2CH_2$). The i.r. spectrum of the crude reaction product indicated that no carboxylic acid was present. The same experiment in THF gave similar result .

2.2 Reaction of Bromomethyltriphenylsilane with Magnesium Powder

A solution of bromomethyltriphenylsilane (0.0026 mole) in dry diethylether (5 ml) was added dropwise to magnesium powder (0.01 mole) After addition was complete the reaction mixture was refluxed with stirring for 12 hours. Dry carbon dioxide gas was passed over the surface of the reaction mixture for 30 min. After hydrolysis, the organic phase was dried over magnesium sulphate and after removal of the ether solvent by evaporation, the yields were methyltriphenylsilane (65%) and 1,2-bis(triphenylsilyl)ethane (34%). The i.r. spectrum of the crude reaction product indicated that no carboxylic acid was present. The same experiment in THF gave similar result.

2.3 The Preparation of Iodomethyltriphenylsilane

Chloromethyltriphenylsilane (6.17 g, 0.02 mole) was refluxed with dry sodium iodide (12g, 0.08 mole) in anhydrous acetone[65] (100 ml) for one week. A white precipitate of sodium salts was removed by filtration and the remaining solution was distilled to remove most of the acetone. Water (50 ml) was added and after extraction with ether, the organic phase was dried over magnesium

sulphate and the ether solvent evaporated. Recrystallisation with light petroleum (60-80°C) yielded 6.7 g (84%), m.p. 112-114°C, (lit.[14] 113-114°C) of iodomethyltriphenylsilane.

^{1}H n.m.r. τ 2.37-2.85 (m,15H, aromatic CH)

τ 7.35 (s,2H,CH_2I)

2.4 Reaction of Iodomethyltriphenylsilane with Magesium Powder

(a) Deuterolysis

A solution of iodomethyltriphenylsilane (1.04 g, 0.0026 mole) in dry diethylether (5 ml) was added dropwise to magnesium powder (0.01 mole) in dry diethylether (2 ml). After addition was complete the reaction mixture was stirred at room temperature for 18 hours, then quenched with excess deuterium oxide. The organic phase was dried over magnesium sulphate and the ether solvent was evaporated leaving the yield of methyltriphenylsilane 0.69 g (97%) m.p. 60-61°C, after recrystallisation from ethanol. The i.r. spectrum of the crude reaction product indicated that no deuterium was present (no peak at IR ν_{max} 2180-2210 cm^{-1} of C-D).

A similar experiment as above was performed by refluxing for 30 minutes only, and a somewhat similar result was obtained.

(b) Carbonation

Triphenylsilylmethyl iodide was reacted as above (a). Dry carbon dioxide gas was passed over the surface of the reaction mixture for 30 minutes. After hydrolysis, the organic phase was dried over magnesium sulphate and after removal of the ether solvent

by evaporation, the yields (from 18 hours stirring at room temperature) were methyltriphenylsilane (70%) m.p. 60-61°C, ^{1}H n.m.r. τ 2.25-2.9 (m,15H, aromatic CH), τ 9.2(s,3H,CH_3) and 1,2-bis(triphenylsilyl) ethane (30%) ^{1}H n.m.r. τ 8.78-8.8 (s,4H,$2CH_2$), 2.25-2.9(m,15H, aromatic CH).

The yields (from 30 minutes at reflux temperature) were methyltriphenylsilane (66.7%) and 1,2-bis(triphenylsilyl)ethane (30%).

The i.r. spectrum of crude reaction product indicated that no carboxylic acid was present (no peak at IR ν_{max} 1670-1700 cm^{-1} of $\geq C = O$).

2.5 Reaction of Iodomethyltriphenylsilane with Johnson Matthey 'Specpure' Magnesium Crystals

Triphenylsilylmethyliodide was reacted as (a) but using Johnson Matthey 'specpure' magnesium crystals instead of magnesium powder for 30 minutes at reflux temperature and deuterolysis as in (a). The yield was methyltriphenylsilane (80-90%). Carbonation as in (b) gave methyltriphenylsilane (68%) and 1,2-bis(triphenylsilyl)ethane (30%).

The i.r. spectrum of the crude reaction product indicated that no deuterium was present in the deuterolysis and no carboxylic acid was present in the carbonation.

3. Reaction of (3-Bromopropyl)triphenylsilane with Grignard Reagents

Grignard reagents were prepared in the conventional manner[7] from alkyl/aryl bromides in diethylether or THF using alkyl/aryl halides: solvent ratio of 1:3 (v/v). For the reactions to be conducted in benzene, the organometallic compounds were initially prepared in diethylether which was then removed by distillation and replaced by benzene until a constant temperature of 76°C was obtained. In all experiments a Grignard reagent: (3-bromopropyl)triphenylsilane molar ratio 2:1 was used and a nitrogen atmosphere was maintained throughout. The following is a typical reaction:-

A solution of n-butylmagnesium bromide (approx. 0.05 mole) in diethylether was filtered free of excess magnesium through an adaptor plug of glass wool to a dropping funnel and then added slowly to a stirred suspension of (3-bromopropyl)triphenylsilane (0.025 mole) in diethylether (20 ml). After refluxing for 48 hours the mixture was hydrolysed with dilute hydrochloric acid and then was washed with sodium bicarbonate and water to remove any acid remained. The organic layer was separated, dried over magnesium sulphate and the solvent was removed carefully by fractionation through a 6 in. column of glass helices. The temperature of the distilling liquid did not rise above 35° throughout the fractionation. NMR analysis of crude yield showed the absorptions of

^{1}H n.m.r.τ2.3-2.8 (m, aromatic CH)
3.9-4.1 (m, 1H)
5.0-5.1 (m,2H)
7.3-7.4 (d, 2H)

8.3-8.8 (m,4H,CH_2)

8.9-9.1 (t,3H,CH_3)

8.60-8.65 (s,6H,CH_2)

TLC was run by using light petroleum/benzene = 9/1 as the eluant. Spots were indicated in positions similar to those of authentic samples of 1,6-bis(triphenylsilyl)hexane and n-propyltriphenylsilane, and other spots were shown corresponding to compounds later separated by column chromatography and identified by spectroscopic technique. The gaseous products were analysed by GLC, as below.

The reaction mixture was then separated into its components by column chromatography using different mixture of light petroleum/ benzene as eluant.

Elution with light petroleum/benzene = 9/1 gave the mixture of n-propyltriphenylsilane (66%) m.p. 83-84°;

^{1}H n.m.r. τ 2.30-2.83 (m,15H, aromatic CH)

8.3-8.88 (m,4H,CH_2)

8.87-9.2 (t,3H,CH_3)

and allyltriphenylsilane (6%) m.p. 87-90°;

^{1}H n.m.r. τ 2.25-2.76 (m,15H, aromatic CH)

3.9-4.4 (m,1H)

4.94-5.21 (m,2H)

7.65 (d,2H, J8Hz)

Elution with benzene gave the mixture of 2:3-benzo-1,1-diphenyl-1-sila-2-cyclohexene (9%) m.p. 77.5-79°C. ^{1}H n.m.r. τ 2.3-2.8 (m,10H, aromatic CH), 3.1-3.5 (m,4H, aromatic CH), 7.8(t,2H,CH_2), 8.4-8.8(m,4H,2CH_2) and 1,6-bis(triphenylsilyl) hexane (8%) m.p. 87-90°;

^{1}H n.m.r. τ 2.30-2.87 (m,15H, aromatic CH),

8.65 (s,6H,CH_2)

Other reactions' separations were similarly performed. The products from (3-bromopropyl)triphenylsilanes with Grignard reagents were separated by addition of a precipitant or by column chromatography and identified using the techniques of TLC, Gas analysis, IR, NMR.

Separation by column chromatography using various mixtures of light petroleum/benzene as eluant gave

(a) biphenyl

(b) mixture of alkyltriphenylsilanes and allyltriphenylsilane,

(c) (3-bromopropyl)triphenylsilane and
(3-phenylpropyl)triphenylsilane,

(d) 2:3-benzo-1,1-diphenyl-1-sila-2-cyclohexene
and 1,6-bis-(triphenylsilyl)hexane.

The individual components of the fractions (a), (b) and (c) were identified by mixed melting point, NMR and IR analyses. The results of the reactions of (3-bromopropyl)triphenylsilane with n-butylmagnesium bromide and phenylmagnesium bromide in different solvents are summarised in Table 1. (p.5a).

3.1 Termination of Grignard Reactions with Deuterium Oxide

Reactions of (3-bromopropyl)triphenylsilanes with n-butylmagnesium bromide in diethylether and in benzene were carried out as described in p.69. When completed, deuterium oxide (10.0 g, 0.5 mole) was added dropwise and the resulting mixture stirred for 30 minutes. Magnesium salts were dissolved by addition of dilute hydrochloric acid (10%, v/v) and the organic phase was washed with sodium bicarbonate solution and water and dried over magnesium sulphate. The products of these reactions were separated and identified as described in p.71-72 (above) and recorded in Table 1. (p.5a).

The relative proportions of deuteriated products were determined from the intensity of the carbon-deuterium absorption in the IR spectrum (2180 cm^{-1}), and from the intensities of the M^+ ions at 302 and 303.

The results of these reactions with Grignard reagents in different solvents and times are summarised in Table 1(p.5a)

4. Reaction of Bromomethyltriphenylsilane with n-Butylmagnesium Bromide

Reaction of bromomethyltriphenylsilane with n-butylmagnesium bromide in diethylether, THF and benzene were carried out in a similar procedure to that of reaction of (3-bromopropyl)triphenylsilane with Grignard reagents, but terminating all the Grignard reactions with deuterium oxide (similar termination in the reactions with (3-bromopropyl)triphenylsilane).

The products of these reactions were separated by column chromatography using light petroleum/benzene as eluant. Separation of the following fractions could be achieved:-

(a) The mixture of n-amyltriphenylsilane and methyltriphenylsilane (Ph_3SiCH_3 + Ph_3SiCH_2D) (eluted with light petroleum/benzene = 9/1).

(b) Bromomethyltriphenylsilane (eluted with light petroleum/benzene = 1/1.)

The individual components of the fractions [(a) & (b)] were determined and identified by NMR.

n-Amyltriphenylsilane m.p. 45-47°

^{1}H n.m.r. τ 2.3-2.8 (m,15H, aromatic CH)

8.4-8.65 (m,8H,CH_2)

9.1 (distorted triplet, 3H,CH_3)

Methyltriphenylsilane m.p. 60-61°

^{1}H n.m.r. τ 2.3-2.8 (m,15H, aromatic CH)

9.2 (s,3H,CH_3)

Bromomethyltriphenylsilane m.p. 120-121°

^{1}H n.m.r. τ 2.3-2.8 (m,15H, aromatic CH)

7 (s,2H,CH_2Br)

The relative proportions of deuteriated product of Ph_3SiCH_2D and Ph_3SiCH_3 were determined from the intensities of the M^+ ions at 274 and 275.

The results of these reactions in diethylether, THF and benzene for 24 hours at room temperature are summarised in Table 2.(p 16)

5. Identification of Reaction Products

Products from the reactions of (3-bromopropyl)triphenylsilane and bromomethyltriphenylsilane with Grignard reagents were identified by comparison with authentic samples (where available) using TLC, gas analysis, GLC and NMR and also from the properties listed below. The elemental analysis and melting points quoted are typical of the samples isolated.

n-Propyltriphenylsilane - m.p. 83-84°(lit.[4] 84°);

^{1}H n.m.r. τ 2.3-2.8 (m,15H, aromatic CH),
8.3-8.87 (m,4H,CH_2),
9.0 (distorted triplet, 3H,CH_3)

Found: C, 83.41; H,7.30. $C_{21}H_{22}Si$
calcd: C, 83.38; H,7.33%)

n-Amyltriphenylsilane - m.p. 45-47° (lit.[66] 47°)

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH),
8.4-8.6 (m,8H,CH_2)
9.1 (distorted triplet, 3H,CH_3).

Methyltriphenylsilane - m.p. 61-62° (lit.[66]63-64°)

^{1}H n.m.r. τ 2.35-2.85 (m,15H,aromatic CH),
9.1-9.2 (s,3H,CH_3)

Triphenylsilanol - m.p. 146-151° (lit.[66]151-153)

^{1}H n.m.r. τ 2.3-2.92 (m,15H,aromatic CH),
7.0 (s,1H,OH).

IR ν_{max} 810 cm^{-1}, 3300 cm^{-1} of -O-H

Allyltriphenylsilane - m.p. 88-90° (lit.[67] 90°)

^{1}H n.m.r. τ 2.25-2.76 (m,15H,aromatic CH),
3.9-4.4 (m,1H),
4.94-5.21 (m,2H)
7.65 (d,2H,J8Hz).

IR ν_{max} 1630 cm^{-1} of C=C
894 cm^{-1} of (CH_2 wag)

2:3 Benzo-1,1-diphenyl-1-sila-2-cyclohexene - m.p. 76-79°(lit.[68] 79°)

^{1}H n.m.r. 2.3-2.8 (m,10H,aromatic CH),
3.1-3.5 (m,4H, aromatic CH),
7.8 (t,2H,CH_2),
8.4-8.8 (m,4H,2CH_2).

A sample was kindly donated by Professor Henry Gilman. The identity of the cyclic compound was established by mixed melting point and comparison of spectra.

1,2-Bis(triphenylsilyl)ethane - m.p. 203-204° (lit.[3] 204-207°)

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH)
8.78-8.8(s,4H,2CH_2)

1,6-Bis(triphenylsilyl)hexane - m.p. 123-125°

^{1}H n.m.r. τ 2.3-2.87 (m,15H,aromatic CH)
8.65 (s,6H,3CH_2)

Biphenyl - m.p. 69-71° (lit.[69] 70°);

IR identical to that of an authentic sample[70]; UV (hexane solution): wavelength of maximum absorption 247 mμ, molar extinction coefficient 19,000 (lit.[62] wavelength of maximum absorption 246 mμ, molar extinction coefficient 20,000).

Butane was analysed by GLC and comparison with retension time of the authentic sample.

Butene was analysed by GLC.

(3-Phenylpropyl)triphenylsilane was not isolated in a pure state but was identified as a component of a mixture from its NMR spectrum,

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH),
8.3-8.8 (m,4H,CH_2)
3.0-3.2 (m,5H,aromatic CH)
6.5 (t,2H,CH_2Ph)

3-d_2-Propyltriphenylsilane - m.p. 83-84° (lit.[4] 84°)

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH)
8.33-8.87(m,4H,CH_2)

IR. ν_{max} 2180 cm^{-1} of C-D.

6. The Determination of Alkyl/Aryl Halides Formation (Halogen Exchange Products) of Reactions between Grignard Reagents and Alkyl/Aryl Halides

Reagent

Neopentyl Bromide was prepared by the method of Sommer and co-workers[72] (prepared from neopentyl alcohol and phosphorus tribromide). Yield 47%, b.p. 105°, n^{20}D 1.4370 (calcd. for $C_5H_{11}Br$: Br,52.9 Found Br,52.9) ^{1}H n.m.r. τ 8.9-9.0 (s,9H,CH_3), 6.7-6.8(s,2H,CH_2Br)

Neopentyl Iodide was prepared by the method of H.N.Rydon[73]. Yield 64-75%; b.p. 54-55°/55 ^{1}H n.m.r. τ 8.9-9.0(s,9H,CH_3), 6.9-7.0(s,2H,CH_2I).

t-Butyl Acetic Acid

A solution of neopentylbromide (15.0 g , 0.0993 mole) in dry diethylether (45 ml) was added dropwise to magnesium metal (2.88 gm, 0.12 mole) in diethylether (5 ml). Reaction was initiated using 2-3 drops of ethylene dibromide and stirring under reflux conditions for 12 hours. Dry carbon dioxide gas was passed over the surface of the reaction mixture for 1 hour at -4° then hydrolysed with dilute hydrochloric acid. The organic layer was separated and dried over magnesium sulphate. Distillation gave 3,3-dimethyl butyric acid (t-butyl acetic acid) 6.26 g(59%); b.p. 94-96°/26 (lit.[63] 96°/26)

^{1}H n.m.r. τ 9.0 (s,9H,CH_3)

7.5-8.0 (s,2H,CH_2CO_2)

Trial experiments indicated that chlorobenzene was a suitable standard for the determination of neopentyl iodide, 1-iodobutane, neopentyl bromide, 1-bromobutane, 2,2,5,5-tetramethylhexane by GLC at the temperatures used.

The reactions between Grignard reagents and alkyl/aryl halides in diethylether are described below.

Grignard reagents used in the experiments were neopentyl magnesiumbromide, n-butylmagnesiumbromide, n-hexylmagnesiumbromide and phenylmagnesiumbromide. They were prepared in the conventional manner[7], using an alkyl halide/solvent ratio of 1/3 (v/v). In all experiments a Grignard reagent: alkyl or aryl halides molar ratio = 2/1, was used and a nitrogen atmosphere was maintained throughout. A typical general reaction is given below.

A solution of neopentylbromide (5 g, 0.033 mole) in dry diethylether (15 ml) was added dropwise to dry magnesium turnings (0.8 g, 0.033 mole). Reaction was initiated using 2-3 drops of ethylene dibromide and stirring under reflux conditions. After addition was complete the reaction mixture was stirred for 12 hours. A solution of neopentylmagnesium bromide was filtered free of excess magnesium to a dropping funnel and then added slowly to a solution of methyliodide (2.5 g, 0.017 mole) in diethylether (5 ml). The mixture was stirred at room temperature for 18 hours, then quenched with dilute hydrochloric acid and water. The organic layer was separated and dried over magnesium sulphate. The solvent was then reduced in volume to 10 ml by careful fractionation through a 6 in. column of glass helices. The temperature of the distilling liquid did not rise above 35° throughout the fractionation. Chlorobenzene (0.5 gm) was added and the mixture was analysed by GLC at 61°. Analysis by GLC indicated the presence of neopentyliodide (0.83 g, 25%) and 2,2,5,5-tetramethylhexane (0.228g, 9.19%) and R_t values are given below:

R_t (mixture) = 17.5, 24.5, 55.5

R_t (neopentyliodide) = 17.5, R_t(chlorobenzene) = 55

Analysis by NMR indicated the presence of neopentyliodide (24%)

^{1}H n.m.r. τ 9.0 (s,9H,$3CH_3$)

7.0 (s,2H,CH_2I)

and 2,2,5,5-tetramethylhexane (9%)

^{1}H n.m.r. τ 9.0 (s,18H,$6CH_3$)

8.85(s,4H,CH_2)

Other reactions of Grignard reagents with alkyl/aryl halides were similarly carried out. The results of similar determinations and similar identifications taken from reactions between n-butylmagnesium bromide and alkyl halides, n-hexylmagnesium bromide and methyl iodide, phenylmagnesiumbromide and methyliodide for different times are recorded in Table 2 (p.16) & Table 7(p.26). The liquid products from the reactions of neopentylmagnesiumbromide with bromomethyltriphenylsilane were determined by GLC. The solid products were crystallised and identified by NMR spectroscopy.

Reaction of Neopentylmagnesium Bromide with Bromomethyltriphenylsilane was carried out as above (p.79). GLC analysis at 61° indicated the presence of 2,2,5,5-tetramethylhexane (25%). The solid product m.p. 119-120° was crystallised and identified by NMR. NMR analysis indicated the presence of Ph_3SiCH_2Br (starting material)

^1H n.m.r. τ 2.30-2.80 (m,15H,aromatic CH)

6.9 (s,2H,CH_2Br)

The Reaction of n-Butylmagnesium Bromide with Methyl Iodide analysed by GLC at 59° which indicated the presence of n-butyliodide (25%) and n-octane (5%) and the R_t values are given below

R_t(mixture) = 28.5, 47.6, 79.3

R_t(n-butyl iodide)= 28.5

R_t(n-octane) = 47

R_t(chlorobenzene)= 79.5

Analysis by NMR indicated the presence of n-butyl iodide (25%).

^{1}H n.m.r. τ 6.7-7.0 (t,2H,CH_2I)

7.95-8.7 (m,2H,-CH_2-)

8.95-9.35(t,2H,CH_3)

and n-octane (5%)

^{1}H n.m.r. τ 8.60-8-9 (s,12H,CH_2)

9.1 (s,6H,CH_3)

The Reaction of n-Butylmagnesium Bromide with Ethyl Bromide

GLC analysis at 59° indicated the absence of n-butyl bromide.

NMR analysis showed the presence of ethyl bromide.

^{1}H n.m.r. τ 6.3-6.75 (q , 2H,CH_2Br)

The Reaction of n-Hexylmagnesium Bromide with Methyl Iodide

GLC analysis indicated the absence of n-hexyl iodide

The Reaction of Phenylmagnesium Bromide with Methyl Iodide

GLC analysis indicated the absence of phenyl iodide.

NMR analysis showed thepresence of methyl iodide.

^{1}H n.m.r. τ 7.8 (s, CH_3I)

and τ 2.4-3.2 (aromatic CH).

6.1 Termination of Grignard Reactions with Deuterium Oxide and Carbon Dioxide

(a) Deuterolysis

Reactions of n-butylmagnesiumbromide with n-octylbromide, neopentylmagnesiumbromide with iodoctane, and n-octylmagnesiumbromide with bromomethyltriphenylsilane were carried out in similar manner, as described in p. 79 , but when completed the reactions were deutrolysed with deuterium oxide (10.0 g, 0.5 mole) instead of hydrolysis with hydrochloric acid and water. The typical general reaction is given below.

n-Butylmagnesiumbromide (approx. 0.033 mole) in diethylether (approx. 15 ml) was added dropwise to a solution of bromooctane (0.017 mole) in diethylether (5 ml). The mixture was stirred under reflux conditions at room temperature for 18 hours. Deuterium oxide (10.0 g, 0.5 mole) was added dropwise and the resulting mixture stirred for 30 minutes. Magnesium salts were dissolved by addition of dilute hydrochloric acid (10% v/v) and the organic phase was washed with sodium bicarbonate solution and water and dried over magnesium sulphate. The solvent was then reduced in volume to 10 ml by careful fractionation through a 6 in. column of glass helices. The temperature of the distilling liquid did not rise above 35° throughout the fractionation. Chlorobenzene (0.3 g) was added and the mixture was analysed by GLC at 100°. Analysis by GLC indicated the presence of n-octane (35%).

Analysis by NMR indicated the presence of $CH_3(CH_2)_6CH_3$ (30%) and $CH_3(CH_2)_6CH_2D$ (5%).

$CH_3(CH_2)_6CH_3$ ^1H n.m.r. τ 8.7 (s,12H,$6CH_2$)

9.11 (s,6H,CH_3)

$CH_3(CH_2)_6CH_2D$ ^1H n.m.r. τ 9.05 (s,3H,CH_3)

9.18 (s,2H,CH_2D) 8.7(s,12H,$6CH_2$)

and ^1H n.m.r. τ 6.5-6.8 (t,2H,CH_2Br) of unreacted bromooctane.

The relative proportions of deuteriated products were determined from the intensity of the carbon-deuterium absorption in IR spectra (2200-2180 cm^{-1}) and estimated from the intensities of the M^+ ions at 114 and 115.

The products of other similar reactions were determined similarly by GLC and identified by the NMR spectra. The relative proportions of deuteriated products were determined from the intensity of the carbon-deuterium absorption in IR spectrum (2200-2180 cm^{-1}) and from the NMR spectra and estimated from the intensities of the M^+ ions at the corresponding compounds.

The results are recorded in Table 8.(p.28).

(b) Carbonation

Reactions of Grignard reagents and alkyl/aryl halides were carried out as described in p. 79 When completed, dry carbon dioxide gas was passed over the surface of the reaction mixture for 30 minutes. After hydrolysis, the organic phase was separated and dried. The ether solvent was then distilled by careful fractionation through a 6 in. column of glass helices. The carboxylic acid products of these reactions were determined by GLC and NMR spectra using propionic acid

as an internal standard for the reactions with methyl iodide and acetic acid as an internal standard for the reactions with ethyl, n-butyl, n-octyl and phenyl halides.

The carboxylic acid yields are recorded in Table 8. (p.28).

The Carbonation Reaction of Neopentylmagnesium Bromide with Methyliodide

Analysis by NMR indicated an intensive peak of acetic acid (15%).

^{1}H n.m.r. τ 7.9 (s,3H,CH_3)

Analysis by GLC at 144° indicated the presence of acetic acid (13%).

R_t(mixture) = 13.9

R_t(acetic acid) = 13.5

The GLC and NMR results of the carboxylation reaction of neopentylmagnesiumbromide with ethyl bromide and ethyl iodide did not show any propionic acid in the final reaction.

The NMR results of the carbonation reactions of neopentylmagnesium bromide with n-butylbromide and n-butyl iodide indicated the presence of valeric acid in amounts 5% and 10% respectively.

^{1}H n.m.r. τ 9.0 (t,3H,CH_3)

8.5 (m,4H,$2CH_2$)

7.65(t,2H,CH_2-CO_2H)

< 0 (s,H,COOH)

The NMR result of carbonation reaction of neopentylmagnesium bromide with n-octyl bromide indicated the absence of nonic acid.

In the carbonation reaction of n-butylmagnesiumbromide and methyl iodide, acetic acid (20%) was formed. This was confirmed by NMR

^{1}H n.m.r. τ 7.9 (s,3H,CH_3)

A similar reaction with ethyl bromide was carried out and the expected product of propionic acid was very small. The percentage value was nearly 3% and confirmed by NMR spectra.

^{1}H n.m.r. τ 7.4-7.5 (q ,2H,CH_2)

8.8 (t,3H,CH_3)

The NMR result showed no benzoic acid was obtained in the carbonation reaction of n-butylmagnesiumbromide with iodobenzene.

6.2 Identification of Reaction Products

The alkyl/aryl halides formation products obtained from reactions between Grignard reagents and alkyl/aryl halides were identified by comparison with an authentic sample (where available) using GLC and also from the properties listed below.

Triphenylsilyl Acetic Acid - m.p. 168-170°(lit.[3] 173-175°)

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH),

7.35 (s,2H,CH_2CO_2) and also a peak appeared at $\tau > 0$ (H,CO_2H)

IR ν_{max} 1650-1700 cm^{-1} of $\rangle C=O$

2800-3300 cm^{-1} of -O-H

2,2-Dimethylbutane b.p. 49-51°

^{1}H n.m.r. τ 9.1 (s,14H)

2,2,5,5-Tetramethylhexane

^{1}H n.m.r. τ 9.0 (s,18H,6CH_3)

8.85 (s,4H,2CH_2)

t-Amyl Bromide

^{1}H n.m.r. τ 8.35 (s,6H,2CH_3)

8.4 (q,2H,CH_2)

9.0 (t,3H,CH_3)

n-Butyl Iodide - b.p. 129-131°

^{1}H n.m.r. τ 6.8 (t,2H,CH_2I)

7.9-8.9 (m,4H,CH_2)

9.1 (t,3H,CH_3)

Ethyl Bromide - b.p. 71-72°

^{1}H n.m.r. τ 8.25-8.45 (t,3H,CH_3)

6.45-6.75 (q,2H,CH_2)

Methyl Iodide - b.p. 41-43°

^{1}H n.m.r. τ 7.8 (s, CH_3I)

Chlorobenzene - b.p. 130-132°

^{1}H n.m.r. τ 2.65-2.9 (m,aromatic CH)

Acetic Acid - b.p. 118°

^{1}H n.m.r. τ 8.0 (s,3H,CH_3)

<0 [200 Hz] (s,H,COOH)

Propionic Acid - b.p. 141°

^{1}H n.m.r. τ 7.65 (q,2H,CH_2)

8.85 (t,3H,CH_3)

Propyl Acetic Acid (Valeric acid) - b.p. 186°/760

^{1}H n.m.r. τ 9.0 (t,3H,CH_3)

8.5 (m,4H,2CH_2)

7.65 (t,2H,CH_2-CO_2H)

<0 (s,H,COOH)

t-Amyl Carboxylic Acid

^{1}H n.m.r. τ 9.1 (t,3H,CH_3)

8.55 (q,2H,CH_2-)

8.8 (s,6H,2CH_3)

<0 [200 Hz] (s,H,COOH).

B. REARRANGEMENT

Reagents

Sodium metal was purchased from Hopkin and Williams Limited.

Sodium Naphthalene solution was prepared by the method of Scott and co-worker[74].

t-Butanol was distilled from sodium metal, immediately prior to use.

Ethanol was dried by the method of Lund and Bjerrum[75].

Hexane was distilled over P_2O_5, immediately prior to use.

Anala R. Methanol was dried by the same method as with ethanol.

1,2-Dimethoxyethane was purified and dried by refluxing and distillation first with sodium metal and then with lithium aluminium anhydride, immediately before use.

Chloromethyltriphenylsilane was prepared by using the method of Huang and co-worker[14], m.p. 113-114°,

^{1}H n.m.r. τ 2.30-2.85 (m,15H,aromatic CH),

6.45-6.5 (s,2H,CH_2Cl)

(3-Chloropropyl)triphenylsilane

Phenyl-lithium (0.3 mole) in anhydrous diethylether (250 ml) was added dropwise to a solution of (3-chloropropyl)trichlorosilane (0.1 mole) in anhydrous ether (20 ml). After addition was completed the reaction mixture was refluxed for 3 hours, quenched with water and the organic phase was separated. The solvent was evaporated and the residue recrystallised from ethanol, yield 60%, m.p. 95-96.5°.

^{1}H n.m.r. τ 2.4-2.8 (m,15H, aromatic CH)

τ 6.43-6.7 (t,2H,CH_2Cl)

τ 7.85-8.35 (m,2H,CH_2)

τ 8.4-8.75 (m,2H,CH_2Si)

Diphenylbenzylbutylsilane

n-Butylmagnesiumbromide (approx.0.11 mole) was added dropwise to a solution of diphenyldichlorosilane (17.71 g, 0.07 mole) in diethylether (20 ml). After addition was completed the reaction mixture was refluxed for 3 hours. Benzylmagnesiumbromide (approx. 0.12 mole) was added to the reaction mixture. The reaction mixture was refluxed for 7 hours, quenched with water and dilute hydrochloric acid. The organic phase was separated and dried over magnesium sulphate. The solvent was evaporated and a yield of diphenylbenzylbutylsilane 18.1 g (78%) was obtained.

NMR analysis showed ^{1}H n.m.r. τ 2.35-2.95 (m,10H,aromatic CH)

τ 3.0-3.4 (s,5H,aromatic CH)

τ 7.4-7.5 (s,2H,CH_2)

τ 8.45-9.45 (m,n-Bu).

Methyl-dihydronaphthalene

Methyl iodide (0.57 g, 0.004 mole) was added to a solution of sodium naphthalene (approx. 0.008 mole) in 1,2-dimethoxyethane (10 ml). The reaction mixture was stirred for 30 minutes at room temperature and then quenched with dilute acetic acid and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the ether gave a crude product of methyl-dihydronaphthalene (63%).

^{1}H n.m.r. τ 2.12-2.41 (m, aromatic CH)
2.43-2.75 (m, aromatic CH)
6.54-6.64 (s,3H,cyclohexene)
6.65-6.75 (s,3H,CH_3)
4.2 (m, 2H, -CH=CH)

1. Reaction of Chloromethyltriphenylsilane with Sodium Metal in Ethanol

A mixture of chloromethyl triphenylsilane (1.55 g, 0.005 mole) and sodium metal (1.2 g, 0.05 mole) in ethanol (45 ml) was refluxed with stirring until all the sodium metal was dissolved ($\sim$ 45 min). Light petroleum (30-40°) was added and the reaction mixture was hydrolysed with water and dilute hydrochloric acid. The aqueous layer was extracted several times with light petroleum and ether. The combined light petroleum and ether extracts were washed with water and dried over magnesium sulphate. Evaporation of the solvents yielded methyltriphenylsilane (34%)

^{1}H n.m.r. τ 9.24 (s,3H,CH_3)

Ph_2SiCh_2Ph rearranged product (15%).

$\underset{R}{|}$

^1H n.m.r. τ 7.4 (s,2H,CH_2Ph)

τ 2.4-2.85 (m,10H, aromatic CH)

τ 2.9-3.1 (s,5H, aromatic CH)

τ 6.6 (s)

$(Ph_3SiCH_2)_2$ 1,2-bis(triphenylsilyl)ethane (14%)

^1H n.m.r. τ 8.78 (s,4H,CH_2)

τ 2.3-2.8 (m,30H,aromatic CH)

2. Reaction of Chloromethyltriphenylsilane with Sodium Ethoxide

Chloromethyltriphenylsilane (1.55 g, 0.005 mole) was added to a solution of sodium ethoxide (sodium 1.2 g, 0.05 mole in ethanol 30 ml) in ethanol (20 ml). The reaction mixture was refluxed for 40-45 minutes. Light petroleum (b.p. 30-40°) was then added to the cooled mixture and hydrolysed with water and dilute hydrochloric acid. The aqueous layer was extracted several times with light petroleum and ether. The organic phase was dried over magnesium sulphate. Evaporation of the solvent yielded chloromethyltriphenylsilane (96%), m.p. 110-111°C).

NMR of the final product is very similar to the starting material chloromethyltriphenylsilane.

3. Reaction of Chloromethyltriphenylsilane with Sodium Metal in t-Butanol

A mixture of chloromethyltriphenylsilane (1.55 g, 0.005 mole) and sodium metal (1.2 g, 0.05 mole) in t-butanol (80 ml) was refluxed with stirring at 40-45° until all the sodium metal was dissolved (∿ 2 days). Light petroleum was added and the reaction mixture was then hydrolysed with water and dilute hydrochloric acid. The aqueous phase was extracted several times with light petroleum (30-40°). The combined light petroleum and ether extracts were dried over magnesium sulphate and evaporated. TLC for the mixture was carried out using light petroleum/benzene = 9/1 as eluant. The corresponding spots and the R_f values were compared with those of authentic compounds.

R_f (mixture) = 0, 0.20, 0.31, 0.36

R_f (Ph_3SiOH) = 0

R_f (Ph_3SiCH_3) = 0.30

R_f (Ph_3SiCH_2Cl) = 0.23

A concentrated sample of the reaction mixture was chromatographed on silica gel using light petroleum/benzene = 9/1 as eluant to give methyltriphenylsilane 0.45 g (35%) m.p. 59-61°.

^1H n.m.r. τ 2.4-2.8 (m,15H, aromatic CH)

τ 9.2 (s,3H,CH_3)

Using benzene as eluant gave 1,2-bis(triphenylsilyl)ethane (2-3%).

^1H n.m.r. τ 8.45-8.9 (s,4H,$2CH_2$).

Using ether as eluant gave the rearranged product $Ph_2\underset{\underset{OH}{|}}{Si}CH_2Ph$ 0.25 g (20%)

^{1}H n.m.r. τ 7.4 (s,2H,CH_2Ph)

τ 7.2-7.3 (s,H,OH)

τ 2.28-2.8 (m,10H,aromatic CH)

τ 2.9-3.1 (s,5H,aromatic CH)

4. An Attempt to Obtain Cleavage of Benzyl Bond from The Product of The Reaction of Chloromethyltriphenylsilane with Sodium Metal in t-Butanol.

A mixture of chloromethyltriphenylsilane (6.1 g, 0.02 mole) and sodium metal (4 g, 0.16 mole) in t-butanol (260 ml) was refluxed at 45-50° with stirring until all the sodium metal dissolved (∿ 4 days). Hydrolysis was carried out as in the above reaction, and a dried concentrated solution of the reaction products was chromatographed on silica gel using light petroleum: benzene = 9.1 as eluant gave methyltriphenylsilane 3:1 g (61%), using benzene as eluant gave 1,2-bis(triphenylsilyl)ethane (3%), using ether as eluant gave the rearranged product $Ph_2\underset{\underset{OH}{|}}{Si}CH_2Ph$) 1.896 g. (32%).

The fraction which was eluted with ether (1.89 g) was boiled with a mixture of ethanol (30 ml) and 50 wt % aqueous sodium hydroxide (4 .5 ml) for 7 hours. Water was added to the mixture followed by ether-extraction. The organic phase was dried over sodium sulphate. The ether was fractionated off and the remaining constituents were analysed.

GLC analysis showed toluene = 0.36 g (20%)

R_t(mixture of EtOH and Toluene) = 0.95, 2.4

R_t(reaction mixture) = 0.9, 2.4

R_t(toluene) = 2.4

R_t(ethanol) = 0.95

Evaporation of ethanol and toluene gave the mixture of octaphenyl-cyclotetrasiloxane and open chain siloxane = 1.13 g (63%).[28]

IR analysis showed ν_{max} = 1020 cm^{-1} and 1180-960 cm^{-1} of Si-O-Si which was very similar to that for the authentic spectra of octaphenyl-cyclotetrasiloxane.[28]

NMR analysis showed ^1H n.m.r. = 2.28-3.2 (m,aromatic CH)

5. Reaction of Chloromethyltriphenylsilane with Sodium t-Butoxide

Chloromethyltriphenylsilane (1.55 g, 0.005 mole) was added to a solution of sodium t-butoxide (sodium metal 1.2g, 0.05 mole, t-butoxide 80 ml). The reaction mixture was refluxed for 2 days (the same time and temperature as the reaction of chloromethyltriphenylsilane with sodium metal in t-butanol). Light petroleum (30-40°) was then added to the cooled mixture and hydrolysed with water and dilute hydrochloric acid. The aqueous phase was extracted several times with light petroleum and ether. The organic phase was dried over magnesium sulphate. A concentrated sample of the reaction mixture was chromatographed on silica gel using light petroleum : benzene = 9:1 as eluant and gave chloromethyltriphenylsilane 0.62 g (43%) m.p. 105-106°, ^1H n.m.r. τ 6.5 (s,2H,CH_2Cl). Using benzene : light petroleum = 1:1 gave 1,2-bis(triphenylsilyl)ethane (1-2%), ^1H n.m.r.τ 8.8(s,4H,$2CH_2$).

Using ether as eluant gave the rearranged product Ph_2SiCH_2Ph (OH) 0.689 g, (47.36%).

^1H n.m.r. τ 7.3-7.6 (distorted s, 2H, CH_2Ph) and (s, H, OH)

τ 2.28-2.8 (m, 10H, aromatic CH)

τ 2.98-3.5 (s, 5H, aromatic CH)

6. Termination of The Reaction between Chloromethyltriphenylsilane and n-Butyllithium in Hexane with Deuterium Oxide

n-Butyllithium in hexane (0.015 mole) was added dropwise to an etheral solution of chloromethyltriphenylsilane (3.1 g, 0.01 mole) cooled to -78°. The stirring was continued for 45 minutes, deuterium oxide (10 ml) was added and hydrolysed with ammonium chloride and then extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the solvent gave chloromethyltriphenylsilane (70%), n-amyltriphenylsilane (6%).

^1H n.m.r. τ 2.4-2.8 (m, 15H, aromatic CH)

τ 8.5-8.85 (m, 8H, CH_2)

τ 8.9-9.2 (distorted triplet, 3H, CH_3)

and 1,2-bis(triphenylsilyl)ethane (6%)

^1H n.m.r. τ 2.4-2.8 (m, 15H, aromatic CH)

8.8 (s, 4H, $2CH_2$)

7. Reaction of Sodium naphthalene with Chloromethyltriphenylsilane

Chloromethyltriphenylsilane (1.86 g, 0.006 mole) was added to sodium naphthalene (approx. 0.008 mole) in 1,2-dimethoxyethane (10 ml). The reaction mixture was stirred for 1 hour at 40° and then quenched with dilute acetic acid, and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the ether gave methyltriphenylsilane (22%), naphthalene (∿ 45-50%). ^{1}H n.m.r. τ 2.2-2.9 (m, aromatic CH). (identical to the authentic sample) and dialkyldihydronaphthalene (26%).

^{1}H n.m.r. τ 2.2-2.9 (m,aromatic CH)
4.2 (s, 2H, -CH=CH-)
6.61 (s, 2H, cyclohexene)
6.8 (s, 6H, $2CH_3$)

8. Reaction of Chloromethyltriphenylsilane with n-Butyllithium and Silver Chloride

Chloromethyltriphenylsilane (3.1 g, 0.01 mole) was dissolved in a mixture of THF (16 ml), diethylether (4 ml) and hexane (4 ml). The mixture was cooled to -78°. n-Butyllithium in hexane (0.015 mole) was added dropwise to the stirred mixture. The stirring was continued for 1 hour at -78°. Dry powdered silver chloride (1.5 g, 0.01 mole) was then added and the reaction mixture stirred for a further 8 hours at -78°. The mixture was then allowed to warm to room temperature and stirred for a further 24 hours. Water was added to the reaction mixture followed by extraction with ether. The ethereal layer was dried over magnesium sulphate and then evaporated. The concentrated

sample of reaction products was chromatographed on silica gel using light-petroleum/benzene = 9/1 as eluant gave methyltriphenylsilane 2.1 gm (37.5%). Using benzene as eluant gave the rearranged product of Ph_2SiCH_2Ph (n-Bu), 0.435 g (8%),

^1H n.m.r. τ 2.24-2.9 (m,10H,aromatic CH)
2.9-3.1 (s,5H,aromatic CH)
7.3-7.4 (s,2H,CH_2Ph)
8.4-9.25 (m,butyl)

and 1,2-bis(triphenylsilyl)ethane 0.234 g, (4%) m.p. 204-206°
and triphenylsilanol 0.141 g (2%) m.p. 142-145°,

^1H n.m.r. τ 2.28-2.9 (m,15H, aromatic CH)
IR ν_{max} 810 cm^{-1} and 3300 cm^{-1} of-O-H.

The fraction eluted with benzene 0.44 g in ethanol (10 ml) was added to a solution of sodium ethoxide (0.003 mole) in ethanol (10 ml). The mixture was refluxed with stirring for 8 hours and hydrolysed with water and dilute hydrochloric acid. Extraction with ether was followed by drying over magnesium sulphate and fractionation of the ether extract. GLC analysis at 150° showed toluene 0.06 g (13%),

R_t (mixture of ethanol and toluene) = 3.5, 4.2
R_t (reaction mixture) = 4.1

Removal of all ethanol and toluene gave Ph_2SiOH (n-Bu) 0.31 g (71%)

^1H n.m.r. τ 2.85-3.0 (m,aromatic CH)
8.6-9.4 (m, butyl)

IR ν_{max} 3300 cm^{-1} of -OH.

9. Reaction of Chloromethyltriphenylsilane with n-Butyllithium, Silver Chloride and Cyclohexene

The reaction was carried out in the same manner described above, (the reaction of chloromethyltriphenylsilane with n-butyllithium and silver chloride), cyclohexene (0.01 mole) was added to the mixture of chloromethyltriphenylsilane and n-BuLi in THF : Et_2O : hexane = 4:1:1 and then silver chloride was added. Yield methyltriphenylsilane (40%), the rearranged product Ph_2SiCH_2Ph (8%) (n-Bu) 1,2-bis(triphenylsilyl)ethane (4%) and triphenylsilanol (2%).

10. Reaction of Chloromethyltriphenylsilane and Cyclohexene with n-Butyllithium

n-Butyllithium in hexane (0.018 mole) was added dropwise to the cooled (0°) mixture of chloromethyltriphenylsilane (0.03 mole) and cyclohexene (0.03 mole) in hexane (5 ml). After addition was completed the reaction mixture was stirred (at 0°) for 1 hour, hydrolysed with water and dilute hydrochloric acid, and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the solvent gave chloromethyltriphenylsilane, m.p. 110-111°C (85%) and NMR showed peak relevant to chloromethyltriphenylsilane.

11. Reaction of (3-Chloropropyl)triphenylsilane with n-Butyllithium and Cyclohexene

n-Butyllithium in hexane (0.01 mole) was added dropwise to the cooled (0°C) mixture of (3-chloropropyl)triphenylsilane (0.02 mole) and cyclohexene (0.02 mole) in hexane (5 ml). After addition was completed the reaction mixture was stirred (at 0°) for 1 hour, hydrolysed with water and dilute hydrochloric acid and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the solvent gave (3-chloropropyl)triphenylsilane (92%), m.p. 93°C,

^{1}H n.m.r. τ 2.4-2.8 (m,15H,aromatic CH)

τ 6.43-6.7 (t,2H,CH_2Cl)

τ 7.85-8.4 (m,2H,CH_2)

τ 8.4-8.75 (m,2H,CH_2Si)

12. Reaction of Chloromethyltriphenylsilane with n-Butyllithium

Chloromethyltriphenylsilane (3.1 g, 0.01 mole) was dissolved in a solution of THF (16 ml), diethylether (4 ml), and hexane (4 ml) at -78°. n-Butyllithium in hexane (0.015 mole) was added dropwise to the mixture for 1 hour at -78° and the reaction mixture stirred for a further 8 hours at -78° and then allowed to warm up to room temperature and stirred for another 24 hours at room temperature. The reaction mixture was hydrolysed with water, dilute hydrochloric acid and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the solvent yielded chloromethyltriphenylsilane (40%) and n-amyltriphenylsilane (20%).

^{1}H n.m.r. τ 2.3-2.8 (m,15H,aromatic CH)

8.4-8.65 (m,8H,CH_2)

9.1-9.2 (distorted triplet, 3H,CH_3)

13. Reaction of Chloromethyltriphenylsilane with Silver Chloride

Chloromethyltriphenylsilane (1.55 g, 0.005 mole) was dissolved in a solution of THF (8 ml), diethylether (2 ml) and hexane (2 ml). The mixture was cooled to -78°C. A dry silver chloride powder (0.75 g, 0.005 mole) was added to the reaction mixture and stirred for 6 hours at -78°C after which it was allowed to warm to room temperature and stirred for a further 19 hours. The reaction mixture was hydrolysed with water and extracted with ether. The organic layer was dried over magnesium sulphate. Evaporation of the solvent yielded chloromethyltriphenylsilane (96%) m.p.110-111°C.

14. Reaction of Chloromethyltriphenylsilane with Potassium - hydroxide and Ethanol

A mixture of chloromethyltriphenylsilane (1.55 g, 0.005 mole) and potassium hydroxide (0.842 g, 0.015 mole) in ethanol (20 ml) was refluxed for 30 hours. The organic layer was dried over magnesium sulphate after hydrolysis with water and extraction with ether. Evaporation of the solvent yielded chloromethyltriphenylsilane (80%) m.p. 110-111° and triphenylsilanol (6%) m.p. 146-148°.

^{1}H n.m.r. τ 2.28-2.8 (m,15H,aromatic CH)

7.0 (s,1H,OH)

IR ν_{max} 810 cm^{-1} of O-H

and 3300 cm^{-1} of O-H.

15. Reaction of Iodomethyltriphenylsilane with Potassium hydroxide and Ethanol

A mixture of iodomethyltriphenylsilane (1.2g, 0.003 mole) and potassium hydroxide (0.2g, 0.0036 mole) in 95% ethanol (20 ml) was refluxed for 1 hour. After hydrolysis with water and extraction with ether, the organic layer was dried over magnesium sulphate. Evaporation of the solvent yielded the rearranged product

$$Ph_2\underset{\underset{R}{|}}{Si}CH_2Ph \text{ (25\%)}.$$

^{1}H n.m.r. τ 2.28-2.8 (m,10H,aromatic CH)
2.9-3.1 (s,5H,aromatic CH)
7.4 (s,2H,CH_2Ph)

and iodomethyltriphenylsilane (70%)

^{1}H n.m.r. τ 2.28-2.8 (m,15H,aromatic CH)
7.3 (s,2H,CH_2I)

and triphenylsilanol (5%)

^{1}H n.m.r. τ 2.28-2.8 (m,15H,aromatic CH)

IR ν_{max} 810 cm^{-1} of O-H
and 3300 cm^{-1} of O-H

C. METALATION OF [$^2H_3$]-METHYLTRIPHENYLSILANE

Reagents. [$^2H_3$]-Methyliodide b.p. 40-41° [lit.[76] 41°] was prepared by the method of Cotton and co-workers[76].

Triphenylchlorosilane was prepared by the addition of phenyllithium to an equimolar solution of dichlorodiphenylsilane and this was then refluxed for 2-3 hours. The solution of the reaction mixture was filtered and distilled off under reduced pressure, and gave triphenylchlorosilane (70%) b.p. 152°/0.3. (lit.[66] 161°/0.6), m.p. 94-98° (lit.[66] 91-111°), ^1H n.m.r. τ 2.28-2.9 (m,15H,aromatic CH).

n-Butyllithium in Hexane was purchased from Ventron Alfa Products and was 1.97 M.

t-Butyl-lithium in Pentane was purchased from Ventron Alfa Products and was 0.75 M.

Tetramethylethylenediamine (TMEDA) was purchased from BDH Chemicals Limited.

1. The Preparation of [$^2H_3$]-Methyltriphenylsilane

A solution of [$^2H_3$]-methyliodide (7.62 g, 0.052 mole) in dry diethylether (20 ml) was added dropwise to magnesium (1.5 g, 0.063 mole) in diethylether (20 ml) with stirring. After the addition was complete, the mixture was stirred at room temperature for 3 hours

and the reaction mixture filtered free of excess magnesium. Triphenylchlorosilane (11.8 g, 0.04 mole) in diethylether (80 ml) was added to the Grignard reagent CH_3MgI deuteriated-methylmagnesiumiodide at 0°C and the mixture stirred at room temperature for 5 days. The mixture was hydrolysed with dilute hydrochloric acid and then washed with sodium bicarbonate and water to remove any remaining acid. The organic layer was separated, dried over magnesium sulphate and the solvent evaporated to give the crude products 10.6 g. The crude products were chromatographed on silica gel using light petroleum/benzene = 9:1 as eluant and gave the white solid of $[^2H_3]$-methyltriphenylsilane Ph_3SiCD_3 9.4 g (84%) m.p. 63-64°C. ^1H n.m.r. τ 2.4-2.8 (m, 15H, aromatic CH). IR ν_{max} 2200-2240 cm^{-1} of C-D.

2. Reaction of $[^2H_3]$-Methyltriphenylsilane with t-Butyl-lithium

A 0.75M solution containing (5.3 ml, 0.004 mole) of t-butyllithium in pentane was added dropwise to a solution of $[^2H_3]$-methyltriphenylsilane (1 g, 0.0036 mole) in THF (6 ml) at -78°C. The reaction mixture was stirred for 2 hours at -78°C. Water and dilute hydrochloric acid were added and the aqueous layer extracted with ether. The organic layer was separated and dried over magnesium sulphate. Evaporation of the solvent yielded $[^2H_3]$ methyltriphenylsilane 0.95 g (95%) m.p. 59-60°, ^1H n.m.r. τ 2.2-2.8 (m,15H,aromatic CH).

3. Reaction of [$^2H_3$]-Methyltriphenylsilane with n-Butyllithium TMEDA

A 1.97M solution containing (2.03 ml, 0.004 mole) of n-butyllithium in hexane was added rapidly to a solution of TMEDA (0.47 g, 0.004 mole) and the mixture was added dropwise to a solution of [$^2H_3$]-methyltriphenylsilane (1 g, 0.0036 mole) in THF (6 ml) at room temperature. The reaction mixture was stirred at room temperature for 12 hours during which time, from an initially colourless mixture, it changed first to light orange then finally became a yellow brown colour. Water and dilute hydrochloric acid were added and the mixture extracted with ether. The organic layer was separated and dried over magnesium sulphate. Evaporation of the solvent yielded [$^2H_3$]-methyltriphenylsilane (70%) m.p.60-62°, ^{1}H n.m.r. τ 2.2-2.8 (m,15H,aromatic CH) and Ph_3SiCD_2-$CH_2CH_2CH_2CH_3$ (30%).

^{1}H n.m.r. τ 2.2-2.8 (m,15H,aromatic CH) and
τ 8.4-9.4 (m,butyl)

4. Reaction of [$^2H_3$]-Methyltriphenylsilane with t-Butyl-lithium TMEDA

A solution of 0.75M t-butyl-lithium in pentane (2.7 ml, 0.002 mole) was added rapidly to a solution of TMEDA (0.23 g, 0.002 mole). The mixture was added dropwise to a solution of [$^2H_3$]-methyltriphenylsilane (0.5 g, 0.0018 mole) in THF (3 ml) at room temperature and the reaction mixture stirred at room temperature for 20 hours. Working up in the usual fashion gave Ph_3SiCD_2H(5-10%) ^{1}H n.m.r. τ 2.28-2.8(m,15H,aromatic CH)
9.1 (s, H,CD_2H)

Ph_3SiCD_2t-Bu (10%) ^{1}H n.m.r. τ 2.28-2.8 (m, 15H aromatic CH)
8.6 (s,9H,-$C(CH_3)_3$).

and [$^2H_3$]-methyltriphenylsilane Ph_3SiCD_3 (80%)

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